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THE BEHAVIOUR OF COPPER ANODES WITH VARIOUS IMPURITY CONTENTS DURING ELECTROREFINING

by

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ABSTRACT

The anodic dissolution of copper anodes having various impurity contents was investigated utilizing potentiodynamic (cyclic-voltammetry) methods. Laboratory conditions were established that resulted in reproducible and predictable electrochemical characteristics for the corrosion of the copper anodes. A strong correlation between the electrochemical behaviour of the copper anodes and their silver content was found. Element surface-region analyses of the copper anodes and investigations of the surface structure were performed to determine the influence of continuous cycling on the surface morphology. Scanning electron microscopy with an energy dispersive X-Ray analysis system was employed to examine the corroded surfaces of the anodes.

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INTRODUCTION

Canada is a major producer of primary copper for both domestic and export requirements. The majority of the copper production comes from the smelting of copper sulphide concentrates. During smelting, many of the impurities contained in the copper concentrates are collected in the blister copper smelter product. Impurities of particular concern include: Ni, Pb, As, Sb, Bi, Se, Te, Ag, Au and the platinum group metals. In order to remove such impurities, electrorefining in a $CuSO_4$ - H_2SO_4 electrolyte is used. In this process, the impure copper is cast into anodes which are electrorefined to yield high-purity (99.99% Cu) copper cathodes. Most of the Ag, Au, Se and Te form insoluble products (anode slimes) during electrorefining, and these products are collected and processed. It is believed that various impurities, or combinations of impurities, have a significant effect on anode passivation and on the morphology and composition of the anode slimes. The problems associated with anode impurities are expected to intensify as anodes become dirtier through the expansion of custom smelting activities (CCR-Noranda), the processing of impurity-rich concentrates (Kidd Creek) or smelter modifications (Inco). If the Canadian copper industry is to remain viable in the face of depressed copper prices and keen international competition, then a reduction in anode passivation that would lower the energy demand, increase current densities and reduce manpower should be addressed and

thoroughly researched.

Despite the large volume of work already reported on the properties and electrochemical behaviour of copper anodes, relatively little research has been done on the effects of impurities, oxygen concentration, electrolyte composition, and operating conditions on the passivation of commercial copper anodes. Recently, Hickling (1) examined several approaches involving the effects of oxygen, selenium and silver on the electrochemical passivation of copper anodes. The Copper 91 - Cobre 91 Conference in Ottawa in August 1991 contained four presentations researching the role of impurities during copper electrorefining. Baltazar and Caissey (2) studied the electrorefining of copper anodes with high silver levels, and concluded that the anode passivation caused by high silver levels can be overcome by careful control of the operating parameters in the tankhouse. Lower copper and nickel concentrations in the electrolyte were found to be effective in alleviating anode passivation during the refining of such anodes. The effect of increasing electrolyte temperature was also researched. Compere, Frechette and Ghali (3) investigated the anodic behaviour of industrial copper anodes in an acidic copper sulphate refining bath and concluded that potentiodynamic, galvanostatic and impedance measurements are complementary and powerful tools for the study of copper passivation. Chen and Dutrizac (4) presented a mineralogical study of anode passivation in copper electrorefining. Detailed mineralogical studies were carried out

on a number of passivated and non-passivated commercial anodes, as well as on several laboratory-passivated anodes, to characterize the phases present and to identify the likely causes of passivation. Nogouchi, Iida, Nakamura and Ueda (5) reported on the behaviour of anode impurities in copper electrorefining and concentrated on the amount of the slime and the slime adhesiveness. They noticed that the passivation increased noticeably with an increased amount of oxygen in the anode, higher current density, and greater concentrations of dissolved oxygen and impurity ions in the electrolyte. The four papers cited above contain numerous references related to the influence of different impurities on the electrochemical behaviour of copper anodes.

Within the framework of the above investigations, a study of the role of impurities on copper anode passivation was undertaken. The preliminary results of this broad research program are outlined in this progress report. The primary objectives of this work are:

1. To improve the economics of the copper electrorefining process by reducing anode passivation.
2. To understand the influence of the impurities contained in copper anodes on the passivation process.
3. To establish a body of fundamental knowledge on anode passivation effects.

EXPERIMENTAL

1. Specific Electrochemical Investigations

The following two areas of research which are of immediate interest with regard to electrochemical passivation and the characterization of impure copper anodes were identified:

1. The effect of silver impurities present in the copper anodes on the polarization behaviour under practical refining conditions.
2. The correlation between surface changes on the corroded anode and the passivation mechanism.

2. Methodology

In the polarization work, cyclic-voltammetry was employed to characterize the formation and reduction of surface species and the reversibility of this process. Morphological aspects of the impure copper anode and identification of reaction products were determined utilizing the scanning electron microscope (SEM) with energy dispersive X-ray analysis (EDX) capabilities.

3. Potentiodynamic Experiments: Cyclic-Voltammetry

To widen the knowledge base on the relationship between the electrochemical behaviour of copper anodes containing different

impurity levels, studies on the formation of a slimes layer under continuous potential cycling were conducted. The first set of potentiodynamic experiments investigated the electrochemical dissolution of copper anodes, containing known amounts of impurities, mainly silver, during potentiodynamic sweeps.

Cyclic-voltammetry was chosen as it is a valuable tool to look at the processes taking place at the electrode surface and, most importantly, the reversibility of those processes as the reaction products accumulate to form a covering layer. Cyclic-voltammetry studies were performed using a conventional water-jacketed cell with a copper anode (prepared in this laboratory) as the working electrode, a platinum counter electrode and a mercury/mercurous sulphate reference electrode. A Luggin capillary, the tip of which was set at a distance of about 1 cm from the surface of the working electrode, was used to minimize uncompensated resistance effects caused by an ohmic drop.

A PAR 173 potentiostat/galvanostat, equipped with plug-in module M 276, was used as a potentiostat allowing the working electrode of the electrochemical cell to be maintained at various programmed potentials with respect to the reference electrode. A PAR voltage function generator provided various potentiodynamic voltage *vs* time programs. I-V profiles were recorded using a Hewlett-Packard X-Y recorder.

All of the cyclic-voltammetry experiments were conducted in aqueous solutions containing 40 g/L Cu and 160 g/L H_2SO_4 at 65°C as these conditions approximate those used in commercial

electrorefining operations. The cell electrolyte was heated and maintained at the desired temperature using a circulating water bath. Experiments were performed in an air atmosphere.

The copper anodes, containing known amounts of impurities, were subjected to a controlled number of continuing cycles ranging between -0.35 V and 0.0 V at a scan speed of 2 mV/s. The anodes were always disconnected at the "cathodic end" of the sweep (at -0.35 V), and usually after 23 or 30 cycles. After removal from the electrochemical cell, each anode was rinsed thoroughly and the excess copper or copper-silver powder was removed very carefully with a tissue. Each anode was then inserted back into the cell and the experiment was continued in the same fashion.

The potential range of -0.35 V to 0.0 V was chosen because of the distinct differences in the electrochemical characteristics displayed by copper electrodes with various impurity contents in this potential region. The scan speed of 2 mV/s was chosen after establishing that the potential at which the peaks form is scan speed dependent.

After the desired experimental conditions were achieved and the experiment was completed, some of the anodes were removed from the cell, immediately rinsed with doubly distilled water, dried and examined under the scanning electron microscope.

The studies presented in this report concentrated on the electrochemical behaviour of copper anodes containing various

amounts of silver. Two other copper electrodes, one containing a high oxygen level and the other containing a high selenium level, were also investigated to compare their electrochemical characteristics with the electrodes containing silver. Copper rods consisting of pure copper, containing varying amounts of silver, oxygen and selenium, were melted and cast by the Noranda Technology Centre. Anodes were prepared by cutting rectangular sections from these copper rods. The compositions of the copper rods are presented in Table 1.

Table 1 - Composition of the Copper Rods Containing Various Amounts of Impurities

Rod No.	Ag %	O_2 %	Se %
20	0.00	0.008	-
21	0.04	0.010	-
6	0.10	0.008	-
22	0.20	0.014	-
7	0.50	0.014	-
8	1.00	0.026	-
5	0.00	1.060	-
11	0.00	0.006	0.95%

RESULTS

The following facts were established in a number of preliminary experiments.

1. Pure copper anodes (no impurities including oxygen) do not easily passivate.
2. The more silver a copper electrode contains, the more readily it passivates.
3. Pure copper electrodes with a high oxygen content passivate easily.
4. Copper electrodes containing selenium passivate easily. Their surface morphology was investigated thoroughly in this laboratory.

Based on this background information, an investigation to correlate the electrochemical behaviour of the copper anodes with their impurity content was launched.

Figure 1 displays a typical cyclic-voltammetry profile of a copper electrode, containing silver, during continuous cycling. In the first cycle (1), there is a long gradual slope, which ends in a gradual curve showing some oscillations in the reverse scan. After several cycles (2), the cyclic-voltammetry profile shows a firmly rounded peak (First Peak). A small sharp peak is formed followed by very heavy oscillations in the reverse scan. As the cycling continues, the transformation of the curve progresses (3). The curve now ends in a very well defined first peak

approximately in the area of the oscillations of the first cycle. The line then goes upwards to form another well defined peak (Second Peak), before turning around at the beginning of the reverse scan. The oscillations move towards more negative potentials, and when the silver content is >0.5%, they disappear altogether.

Examination of Figure 1 demonstrates that the cyclic-voltammogram of a copper electrode containing silver, recorded in the potential range between -0.35 V and 0.0 V, consists of five distinct regions, which are marked A to E on the figure.

(A) - copper dissolution where the current is proportional to the voltage,

(B) - formation of the first peak,

(C) - a second peak starts to develop with time, and as more silver powder accumulates on the electrode surface. At the same time, the first peak shifts towards more negative potentials,

(D) - oscillations,

(E) - regular dissolution curve re-established along the same slope as the initial dissolution.

As a result of continuous cycling, the anodic current decreases dramatically. The surface of the anode is covered with a mixture of copper and silver powder, or exclusively with silver powder for high silver content electrodes.

Figures 2-9 display the cyclic-voltammetry profiles of several electrodes investigated in the course of this research.

Each figure shows the average performance of individual electrodes; every measurement was repeated several times in order to achieve full reproducibility of electrochemical behaviour.

DISCUSSION

Hypothesis

For anodes containing silver the sooner the second peak develops (during continuous cycling), the faster the electrode passivates.

As was stated above, previous results proved that the time required for an electrode to passivate is related directly to the silver content of the electrode. It was established in the course of the current research that the silver content of the electrode determines how soon the second peak forms. This suggests that the number of continuous cycles needed to form the second peak can be directly correlated with the ease of passivation.

In fact Table 2 shows the correlation between the silver content of the electrode and the number of cycles required to "grow" the second peak.

Table 2 - Number of Cycles Required to Develop the Second Peak

Rod No.	Impurity Content	No. of cycle when the peak appears for the first time
20	0.00% Ag	no peak, just oscillations
21	0.04% Ag	23
6	0.10% Ag	6
22	0.20% Ag	5
7	0.50% Ag	3
8	1.00% Ag	2
5	0.00% Ag, 1.06% O_2	6
11	0.00% Ag, 0.95% Se	6

Figures 10-17 demonstrate the cyclic-voltammetry profiles taken during the tenth cycle of continuous cycling. Each figure represents an electrode containing a different level of impurities. Depending on the silver content, the cyclic-voltammetry profile shows either one peak (pure copper), one peak followed by heavy oscillations (0.04% silver), two well defined peaks followed by oscillations (0.1 and 0.2 % silver; also oxygen and selenium as impurities), or two well defined peaks with no oscillations (0.5% and 1.0% silver).

By combining these experimental results with the visual observation of the working anodes, some of the electrochemical phenomena can be explained. For pure copper (low oxygen) and copper anodes containing 0.04% Ag, many copper flakes separate from the electrode surface every time the cyclic-voltammogram passes through the oscillation stage, regardless of where on the scan the oscillations occur. Copper anodes containing higher silver levels, as well as those containing high oxygen and selenium levels, do not result in flake formation during the final phase of oscillation. The electrochemical reaction products produced in the forward scan stay on the surface during the reverse scan, though they are loosened during the reverse scan (heavy oscillations). As more reaction products accumulate and the surface layer grows thicker, a secondary surface forms that displays its own characteristics which are different from those of the primary surface now hidden underneath.

Careful examination of the cyclic-voltammetry profiles

indicates a definite difference in the electrochemical characteristics of copper electrodes containing silver and those containing high oxygen and selenium levels. All of the electrodes which contain silver displayed similar current density characteristics with a "First Peak" at approximately 360 mA/cm^2. The electrodes containing high oxygen and selenium levels were characterized by separate current density ranges and distinct cyclic-voltammetry profiles.

The idea of a secondary, electrochemically active surface formed on the original primary surface was examined by removing the cycled anodes, rinsing them, and in some cases, cleaning them very gently with a tissue. This procedure ensured the removal of much of the copper and silver powder without damaging the actual surface of the anode. The electrodes were then re-immersed in the electrolyte and the measurements continued. The difference between the cyclic-voltammetry profiles of a slime-covered electrode and a cleaned electrode was significant. Figures 18, 19 and 20 show cyclic-voltammetry profiles of three anodes containing different amounts of silver (0.04%, 0.1% and 0.2%) that were taken (A) before cleaning, and (B) after cleaning. Partial elimination of the secondary surface layer resulted in a dramatic increase in the anodic current and in a complete change of the electrochemical profile of the anode. It seems that the "second peak" is associated with the amount of material accumulated on the surface. Figures 21 and 22 present the electrochemical "before and after" profiles of electrodes

containing 0.5% and 1.0 % silver, respectively. The first profile recorded after rinsing, although different from the profile before rinsing, shows clearly that there was a substantial amount of silver left on the surface. The residual silver shows its presence in the form of a small sharp peak formed during the reverse scan. The high silver-content copper anodes generate a large amount of silver powder on the surface that is extremely difficult to remove completely; hence the amount of silver left on the surfaces of these cleaned anodes was still substantial.

The "conditioning" effect of cycling on the surface of the electrode is puzzling. The surface of a corroded anode which had been previously cleaned does not produce the "second peak" as quickly as a freshly polished surface. Figures 23, 24 and 25 compare the electrochemical behaviour of electrodes which were subjected to 23-30 continuous cycles, cleaned, and subjected to more continuous cycles. In some cases (Figure 26), it was observed that the cleaned electrodes displayed a remarkable resistance to growing any peaks, and showed a linear I-V characteristic of copper dissolution. The anode dissolved without producing any copper or silver powder on its surface for many cycles.

It seems that the surface conditioning effect depends on:

- how much silver the copper electrode contains,
- how many cycles the electrode was subjected to,
- the potential range used.

If the hypothesis correlating the ease of formation of the second peak with the readiness of an electrode to passivate is correct, then by modifying the factors which cause the "Second Peak" it might be possible to reduce anode passivation. Therefore, it may be possible to reduce ancde passivation by employing an electrochemical pretreatment or conditioning technique.

SEM INVESTIGATIONS

Preliminary SEM studies were performed to examine the surface morphology of the copper anodes at different stages of the electrochemical process. The initial investigations compared the surface morphologies of pure copper anodes and copper anodes containing 1.06% oxygen that were subjected to identical electrochemical treatment. Figure 27 shows the polished surfaces of: (a) the pure copper anode and (b) the copper anode containing 1.06% oxygen. The polished surface of the oxygen-containing anode shows many large cavities probably related to the more brittle nature of the impure copper. The morphologies of the surfaces of those two electrodes after they were subjected to continuous cycling (40 cycles) are presented in Figure 28 (a) and (b). In both cases the anodes were removed from the experimental cell and carefully rinsed with distilled water to remove copper powder and other reaction products prior to examination under the scanning electron microscope. There is a definite difference

between the surface structures of these two electrodes. The pure copper anode (a) shows randomly distributed holes and cavities. The high-oxygen copper anode displays a definite pattern of segments filled with holes of different shapes (b). The pattern is more clearly illustrated under higher magnification in Figure 29, and seems to be related to the original Cu-Cu_2O eutectic structure of the anode. Although both electrodes display a different surface morphology both contain cubo-octahedral holes, probably due to the crystallographic dissolution of copper or to the simple dissolution of Cu_2O crystal inclusions (Figure 30 (a) and (b)). For comparison, a secondary electron micrograph of an unwashed high-oxygen anode is presented in Figure 31. The entire anode is covered with copper sulphate which masks the surface structure. The characteristic small holes that are a part of the previously described pattern are, however, clearly visible. Some secondary electron micrographs were taken of the unwashed surface of the 0.5% silver-containing copper anode after 30 continuous cycles. Unfortunately, there is not much to see as silver powder and copper sulphate cover the entire surface (Figure 32).

FUTURE EFFORTS

The polarization/passivation of the copper anodes containing various impurities during a controlled electrochemical process was the subject of this stage of work. A strong correlation between the electrochemical behaviour of the copper anodes and

their impurity content was found. The "conditioning" effect of cycling on the surface of the anode was discovered. Preliminary SEM studies were performed to characterize the surface morphology of the partially dissolved copper anodes.

As an extention of this investigation, the following studies should be performed to define the possibility of preventing anode passivation using electrochemical methods:

1. Establish an environment for the surface pretreatment or conditioning to reduce or eliminate anode passivation.
2. Carry out passivation studies to compare the electrochemical passivation (passivation time) of freshly prepared electrodes containing different impurity contents and the passivation time of preconditioned but otherwise identical electrodes.
3. Perform morphological studies of the copper anode surfaces at different stages of the potentiodynamic measurements.

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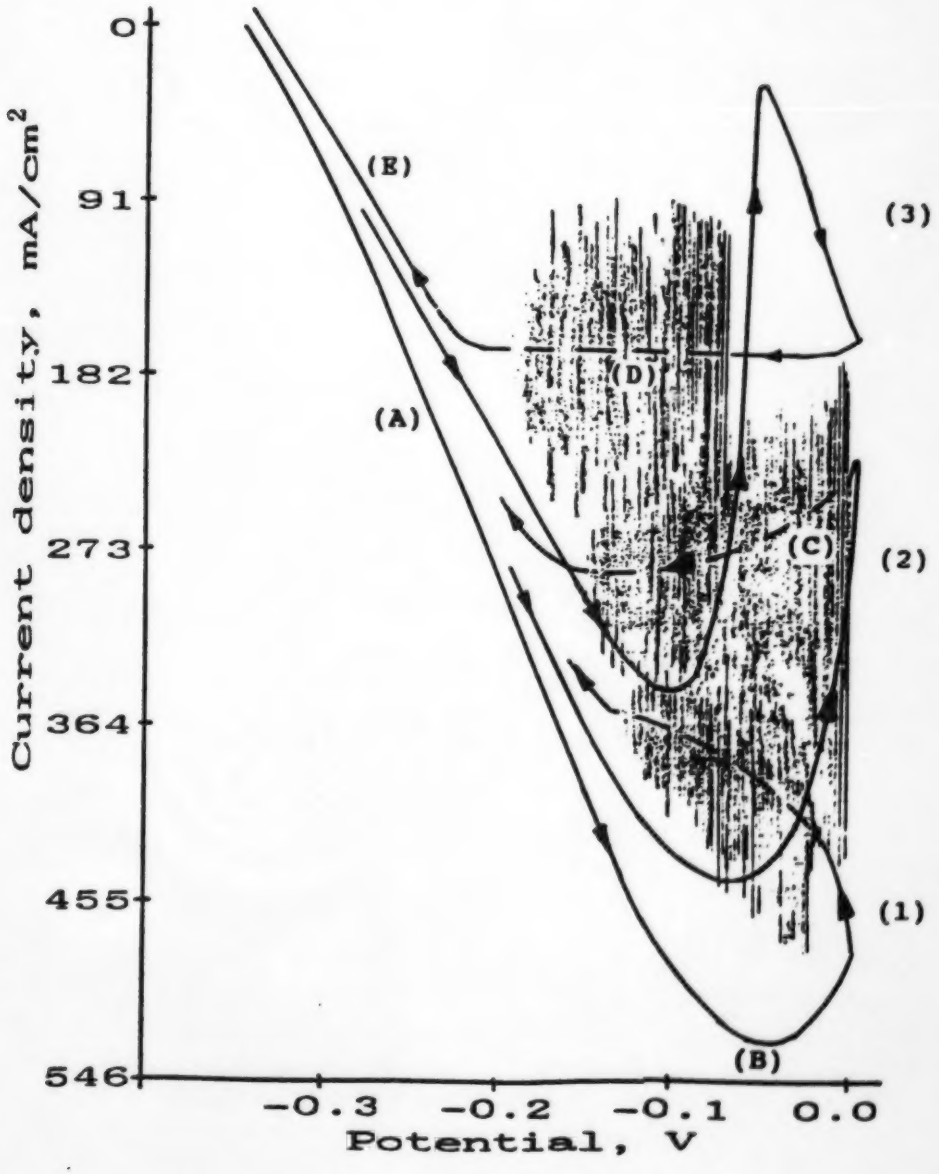


Fig. 1. The formation of peaks during the cycling of coppe electrodes containing different amounts of silver (rod No. 6 where: (1) first cycle, (2) 4th cycle and (3) 23rd cycle).

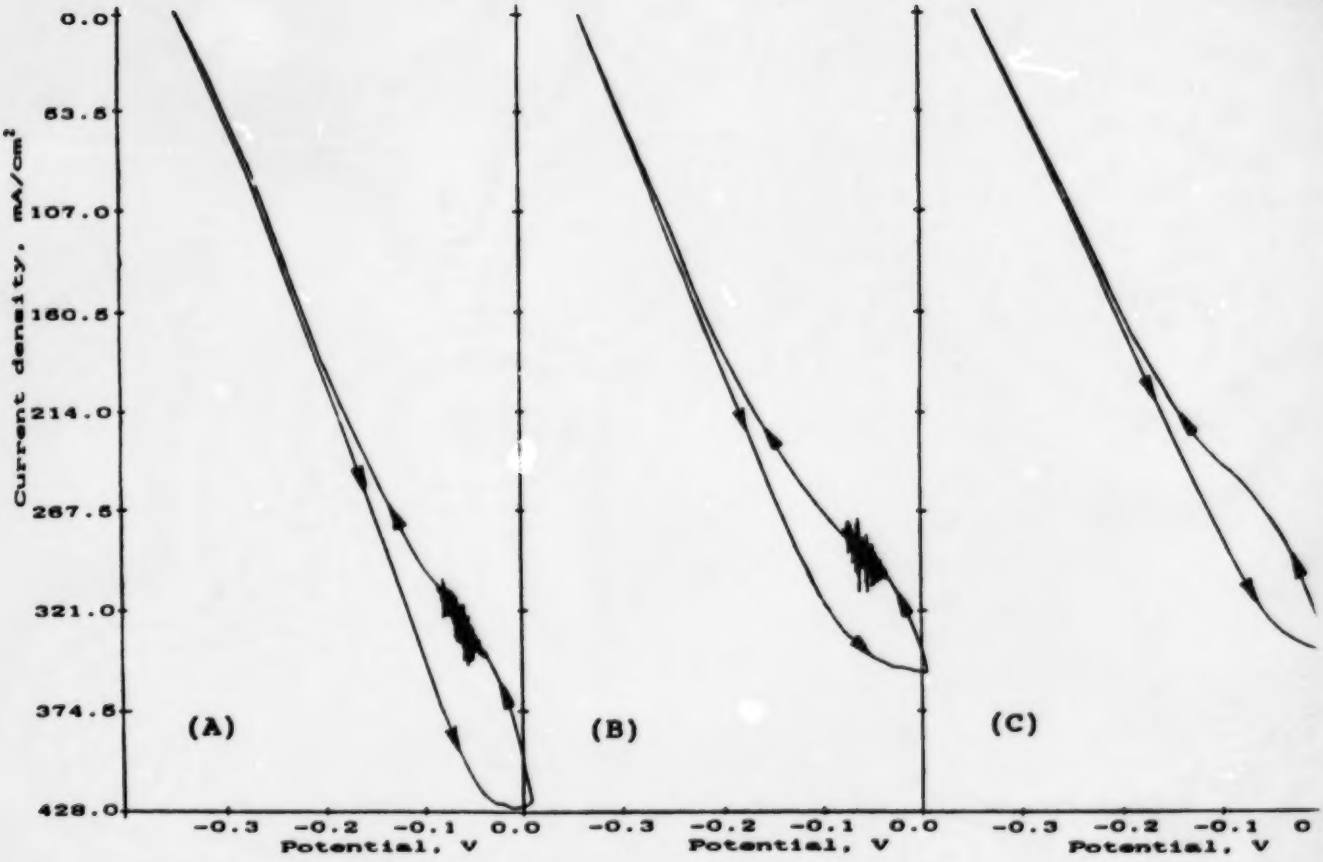


Fig. 2. Cyclic-voltammogram of the pure copper anode (rod No. 20) recorded during continuous cycling, where: (A) first cycle, (B) 4th cycle and (C) 23rd cycle.

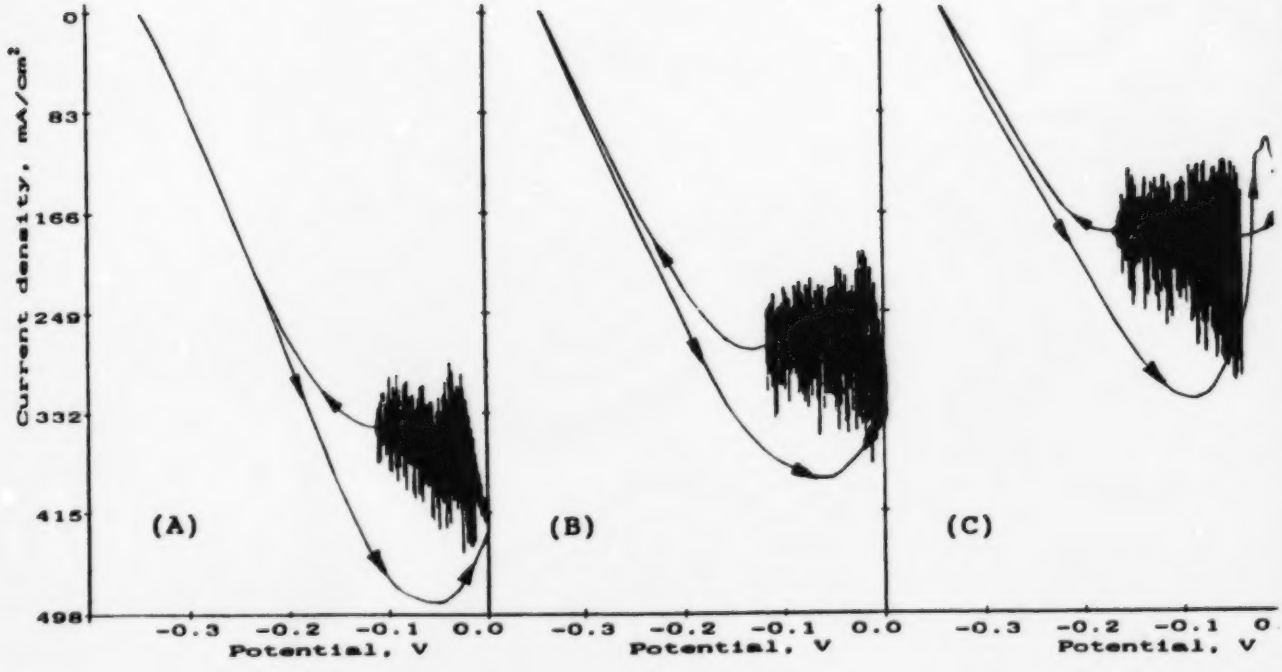


Fig. 3. Cyclic-voltammogram of the copper anode containing 0.04% Ag (rod No. 21) recorded during continuous cycling, where: (A) first cycle, (B) 10th cycle and (C) 30th cycle.

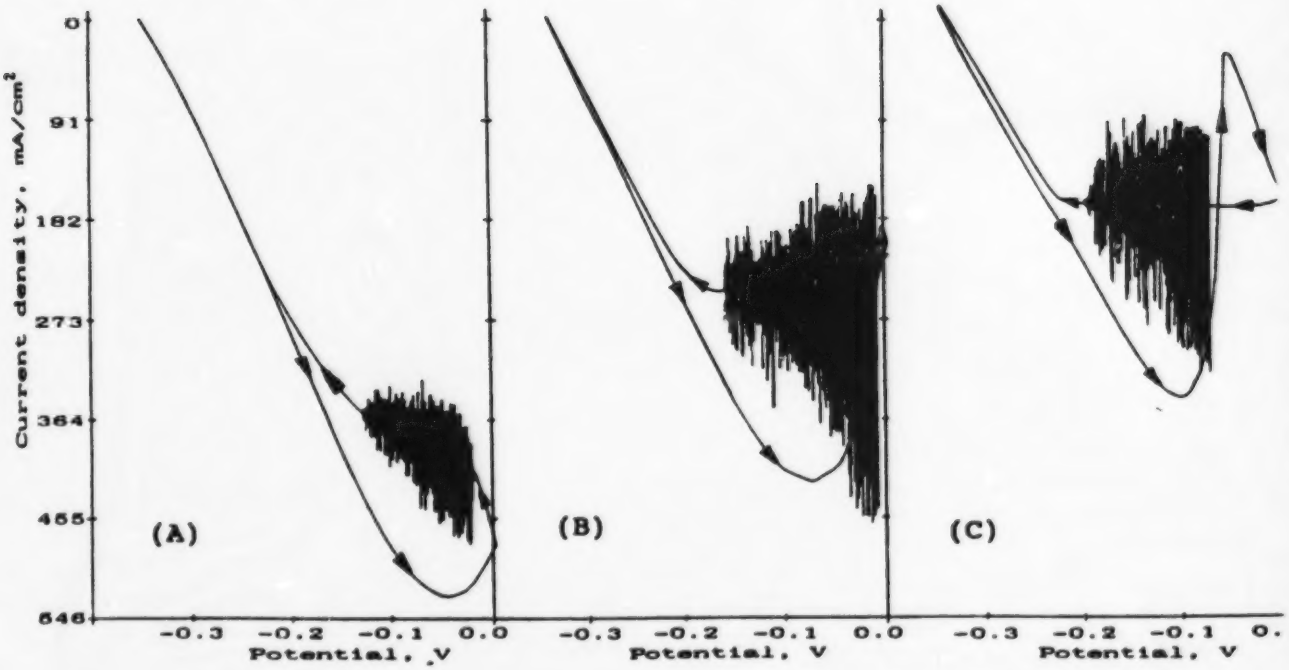


Fig. 4. Cyclic-voltammogram of the copper anode containing 0.1% Ag (rod No. 6) recorded during continuous cycling, where: (A) first cycle, (B) 6th cycle and (C) 23th cycle.

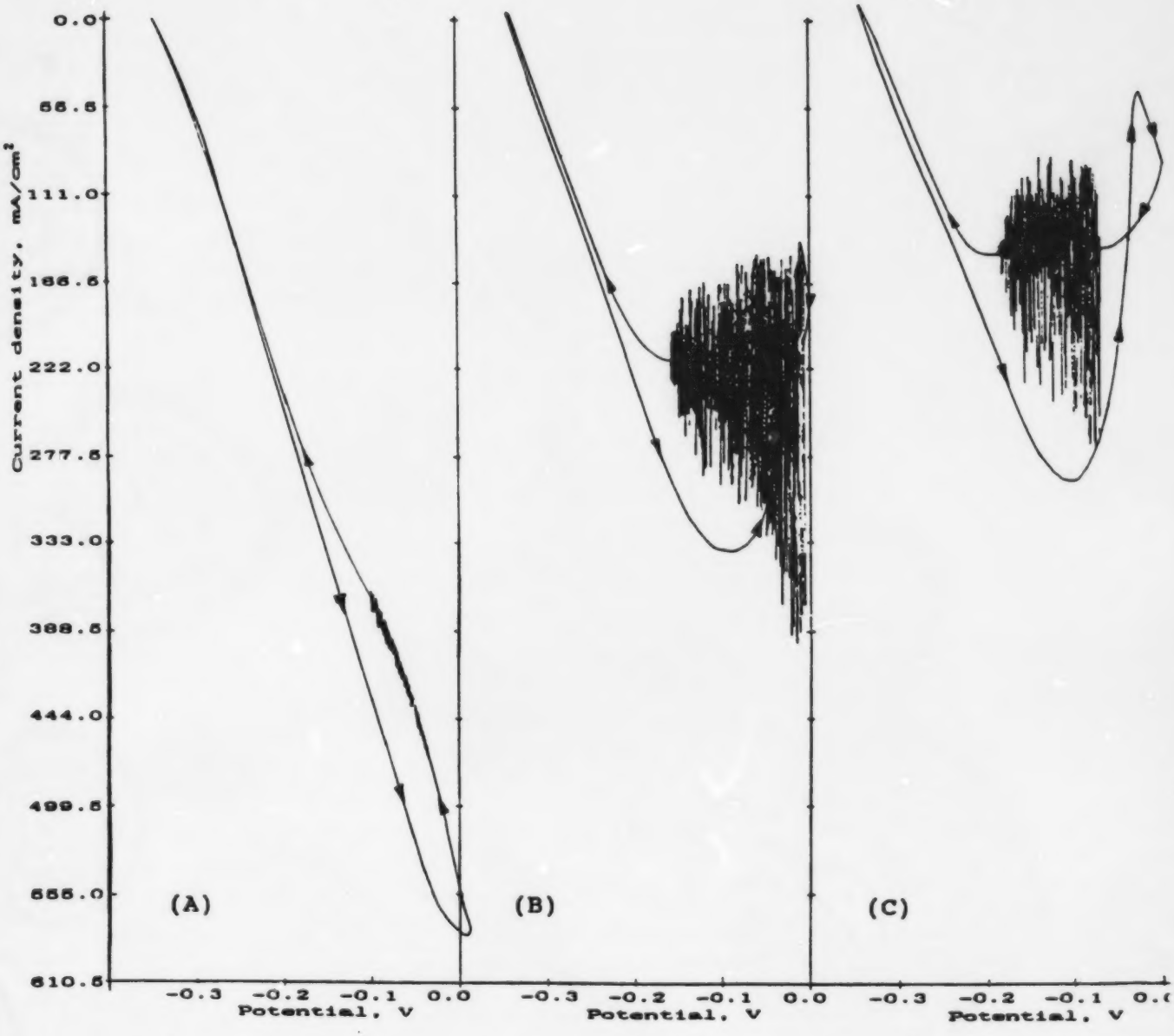


Fig. 5. Cyclic-voltammogram of the copper anode containing 0.2% Ag (rod No. 22) recorded during continuous cycling, where: (A) first cycle, (B) 6th cycle and (C) 23th cycle.

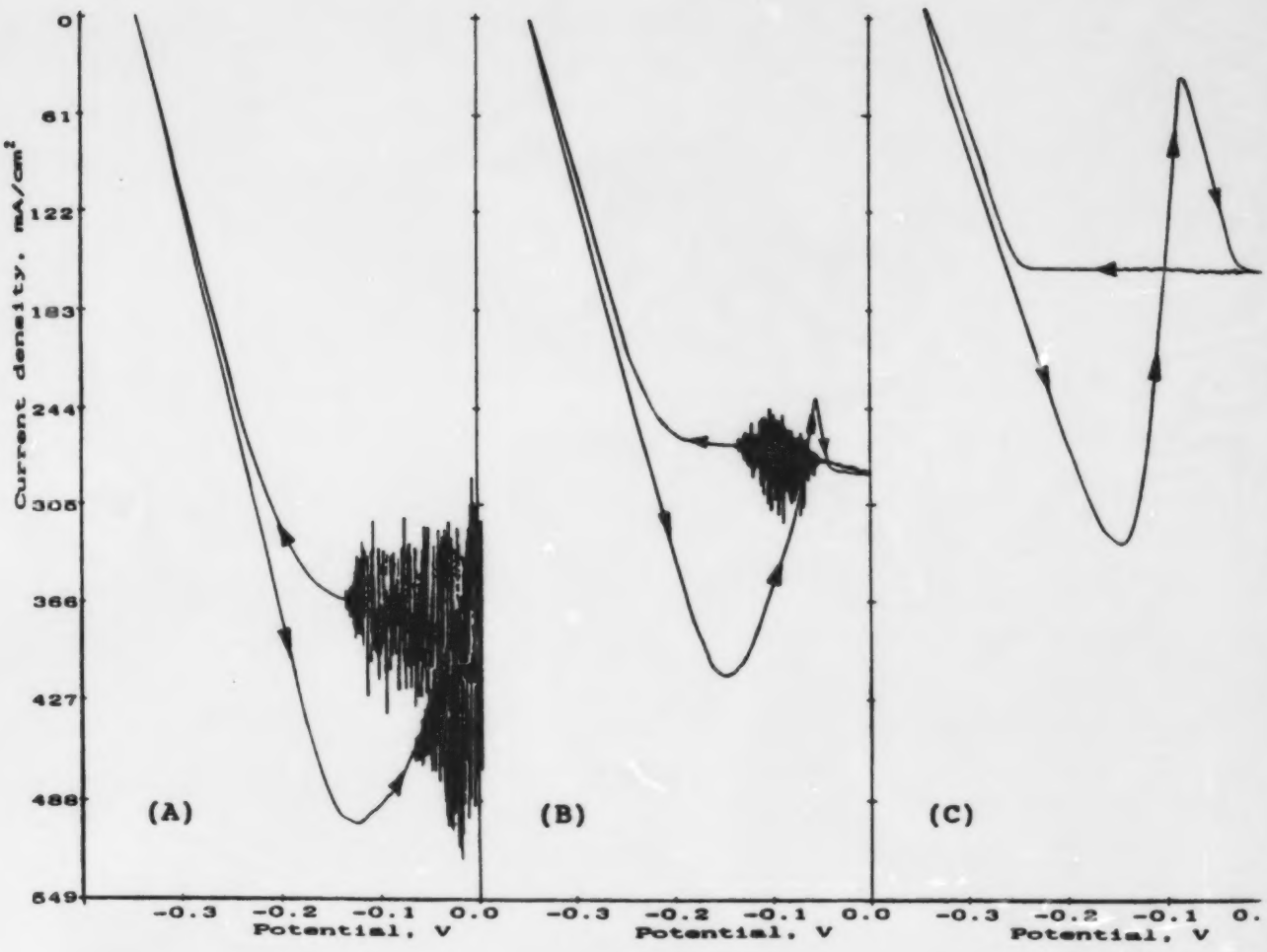


Fig. 6. Cyclic-voltammogram of the copper anode containing 0.5% Ag (rod No. 7) recorded during continuous cycling, where: (A) first cycle, (B) 4th cycle and (C) 23th cycle.

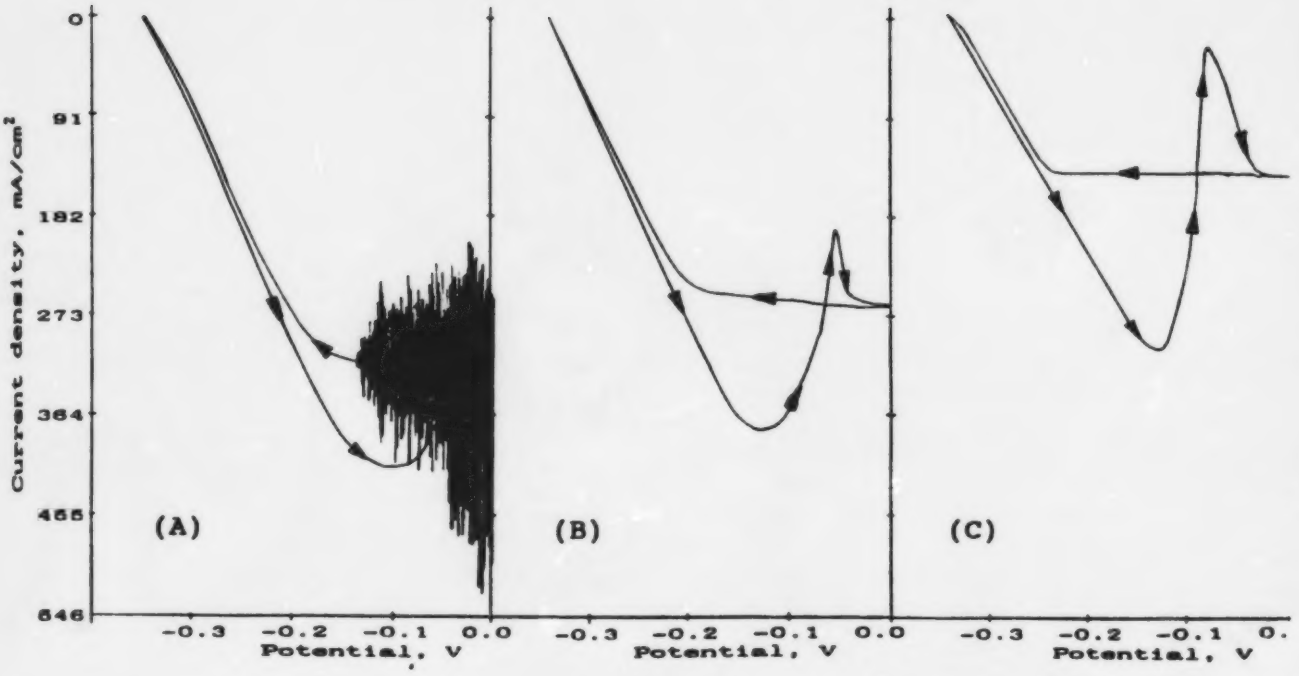


Fig. 7. Cyclic-voltammogram of the copper anode containing 1.0% Ag (rod No. 8) recorded during continuous cycling, where: (A) first cycle, (B) 4th cycle and (C) 23th cycle.

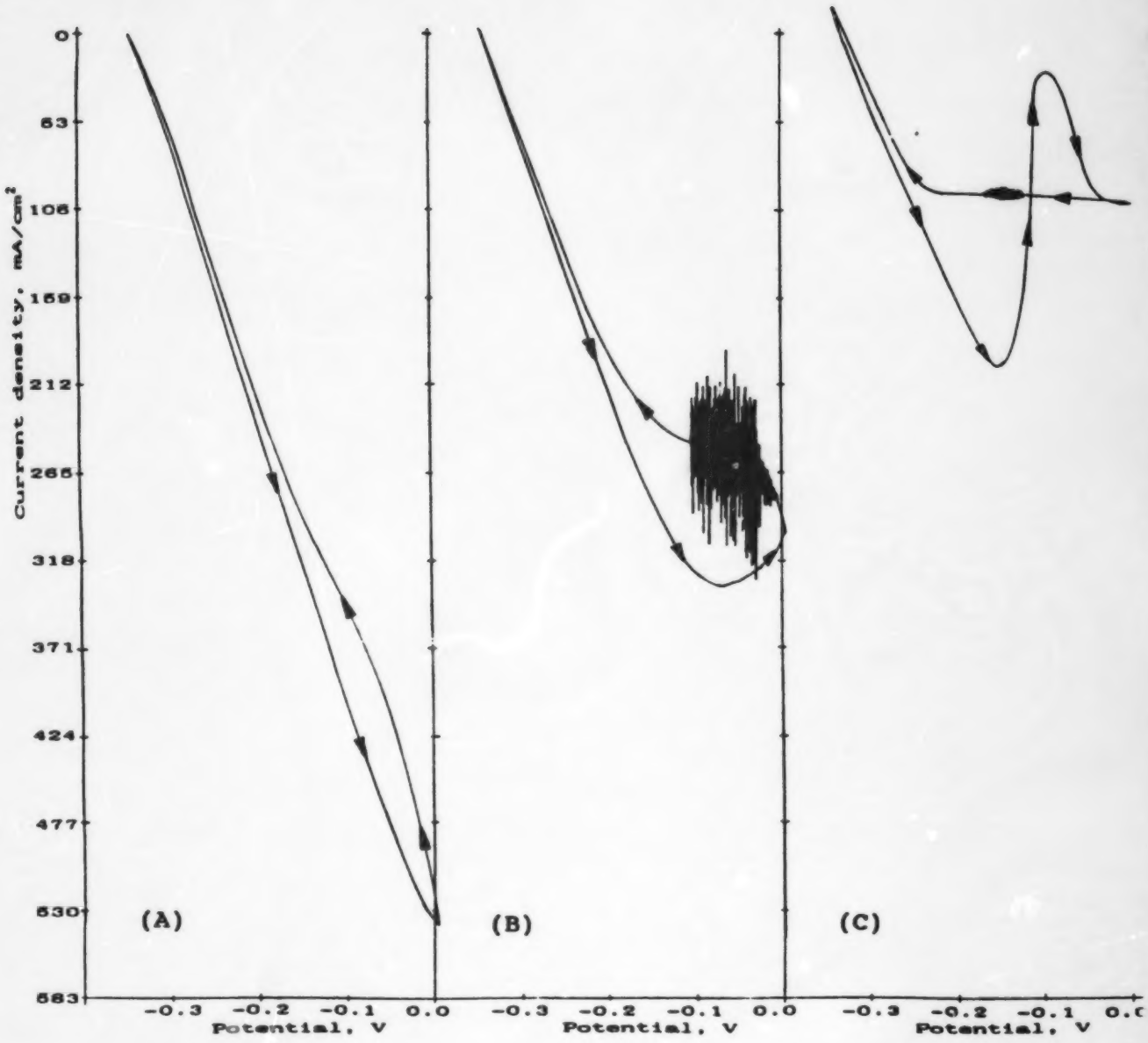


Fig. 8. Cyclic-voltammogram of the copper anode containing 1.06% O_2 (rod No. 5) recorded during continuous cycling, where: (A) first cycle, (B) 4th cycle and (C) 26th cycle.

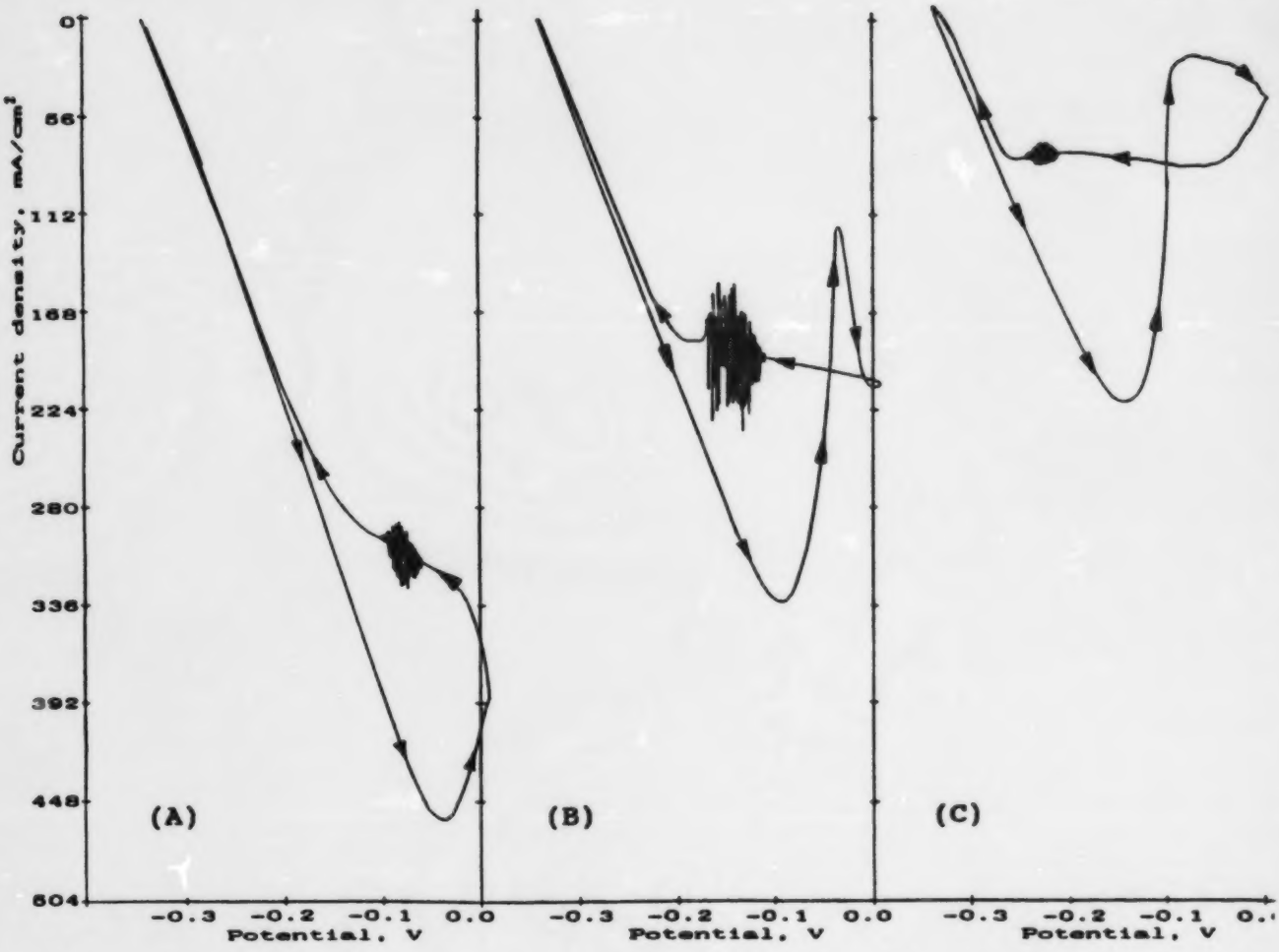


Fig. 9. Cyclic-voltammogram of the copper anode containing 0.95% Se (rod No. 11) recorded during continuous cycling, where: (A) first cycle, (B) 4th cycle and (C) 25th cycle.

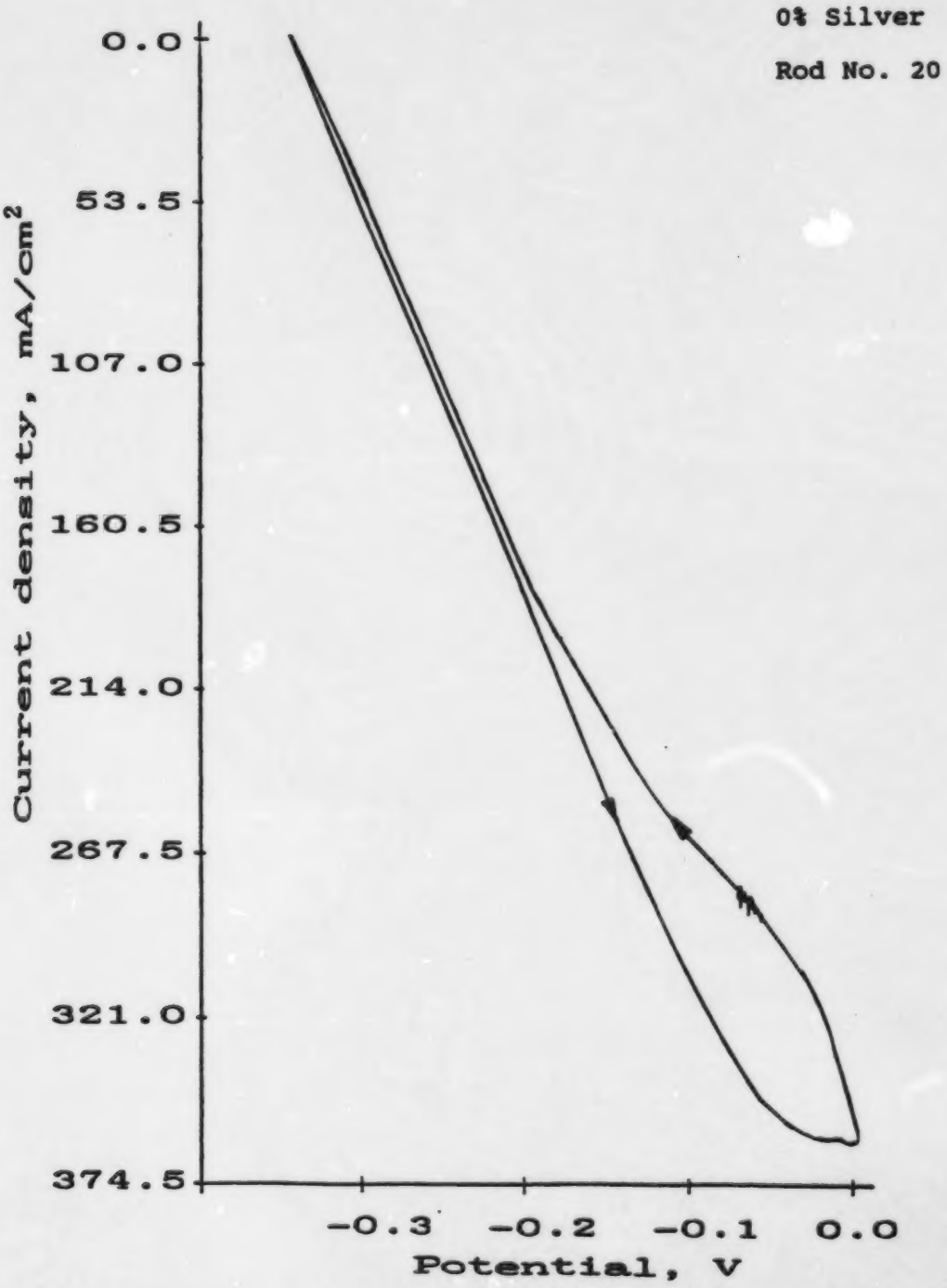


Fig. 10. The cyclic-voltammetry profile of the tenth cycle recorded during continuous cycling.

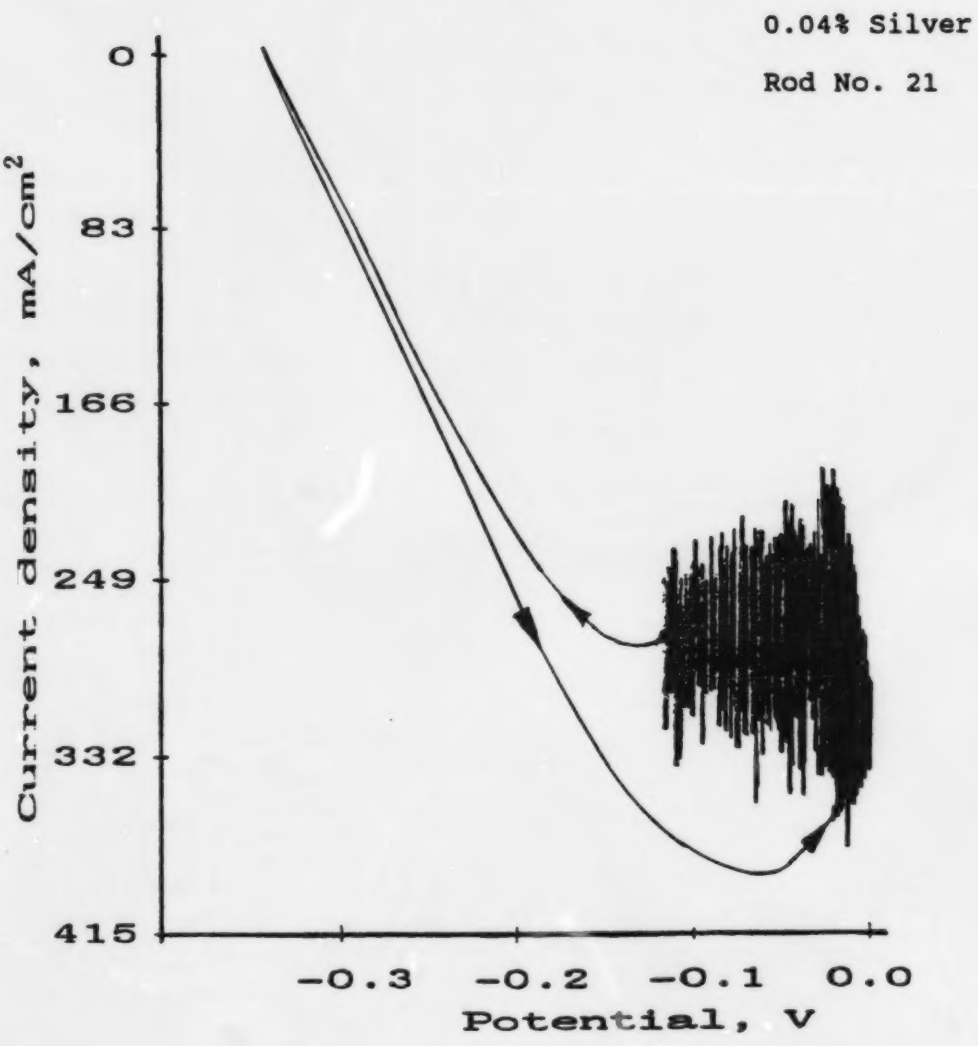


Fig. 11. The cyclic-voltammetry profile of the tenth cycle recorded during continuous cycling.

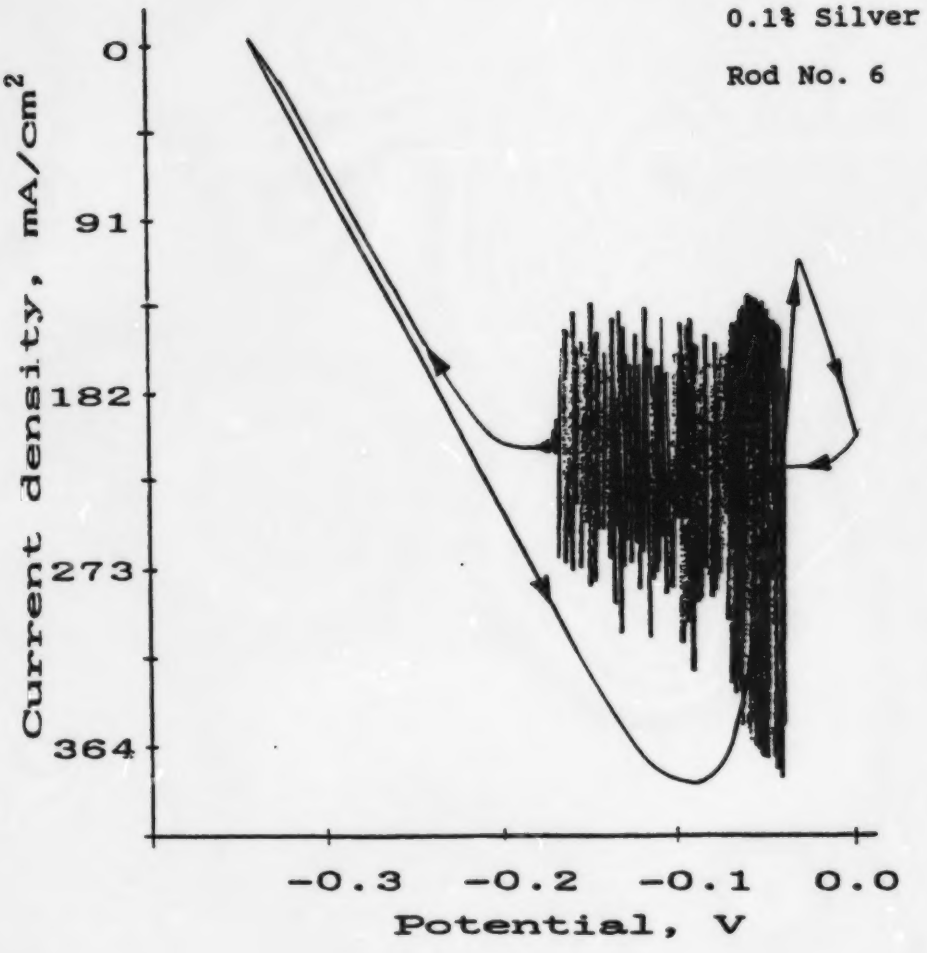


Fig. 12. The cyclic-voltammetry profile of the tenth cycle recorded during continuous cycling.

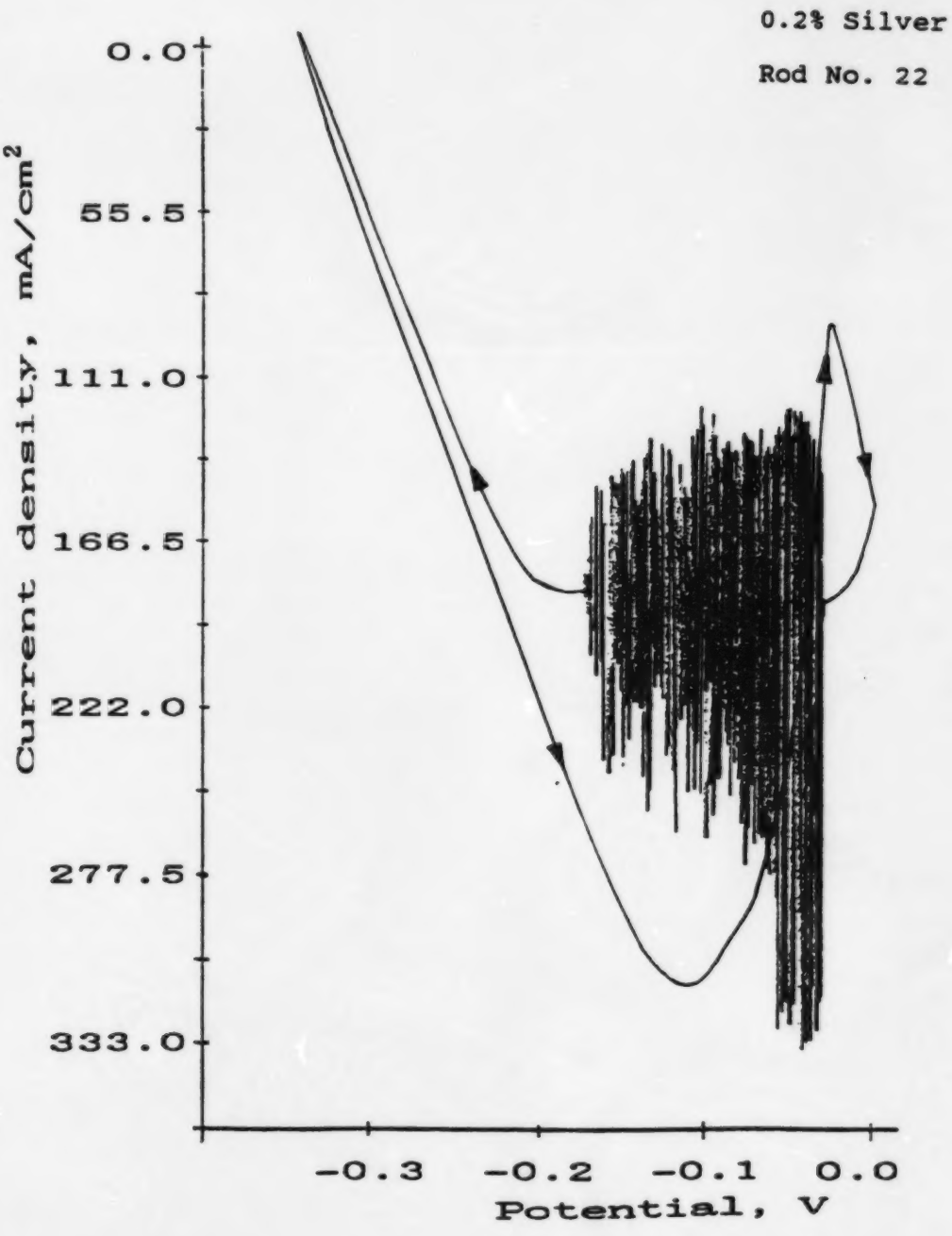


Fig. 13. The cyclic-voltammetry profile of the tenth cycle recorded during continuous cycling.

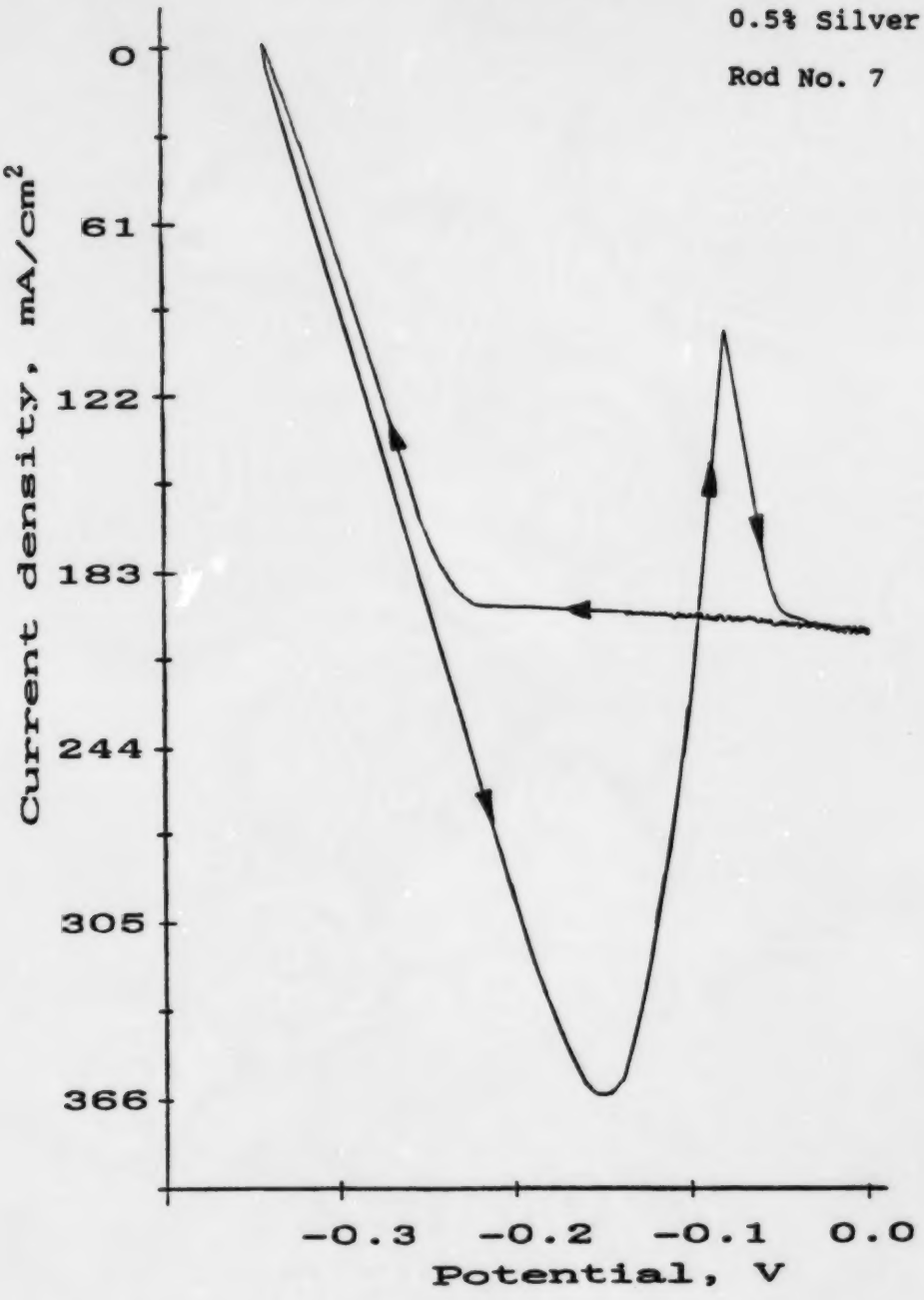


Fig. 14. The cyclic-voltammetry profile of the tenth cycle recorded during continuous cycling.

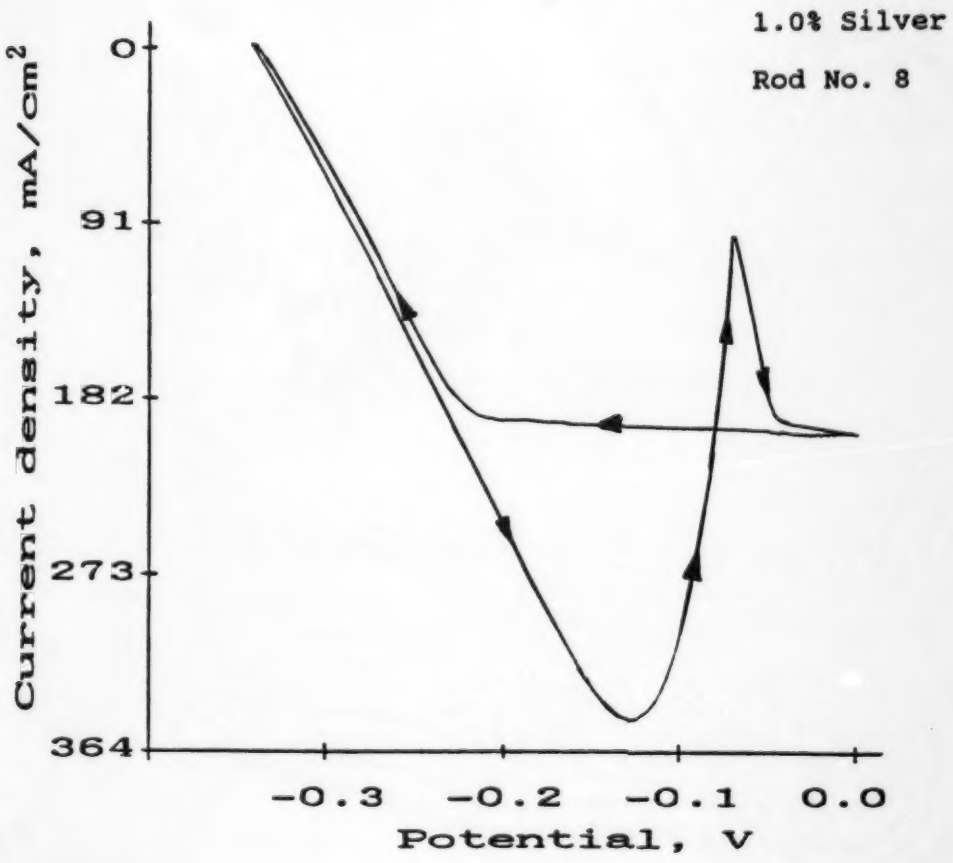


Fig. 15. The cyclic-voltammetry profile of the tenth cycle recorde during continuous cycling.

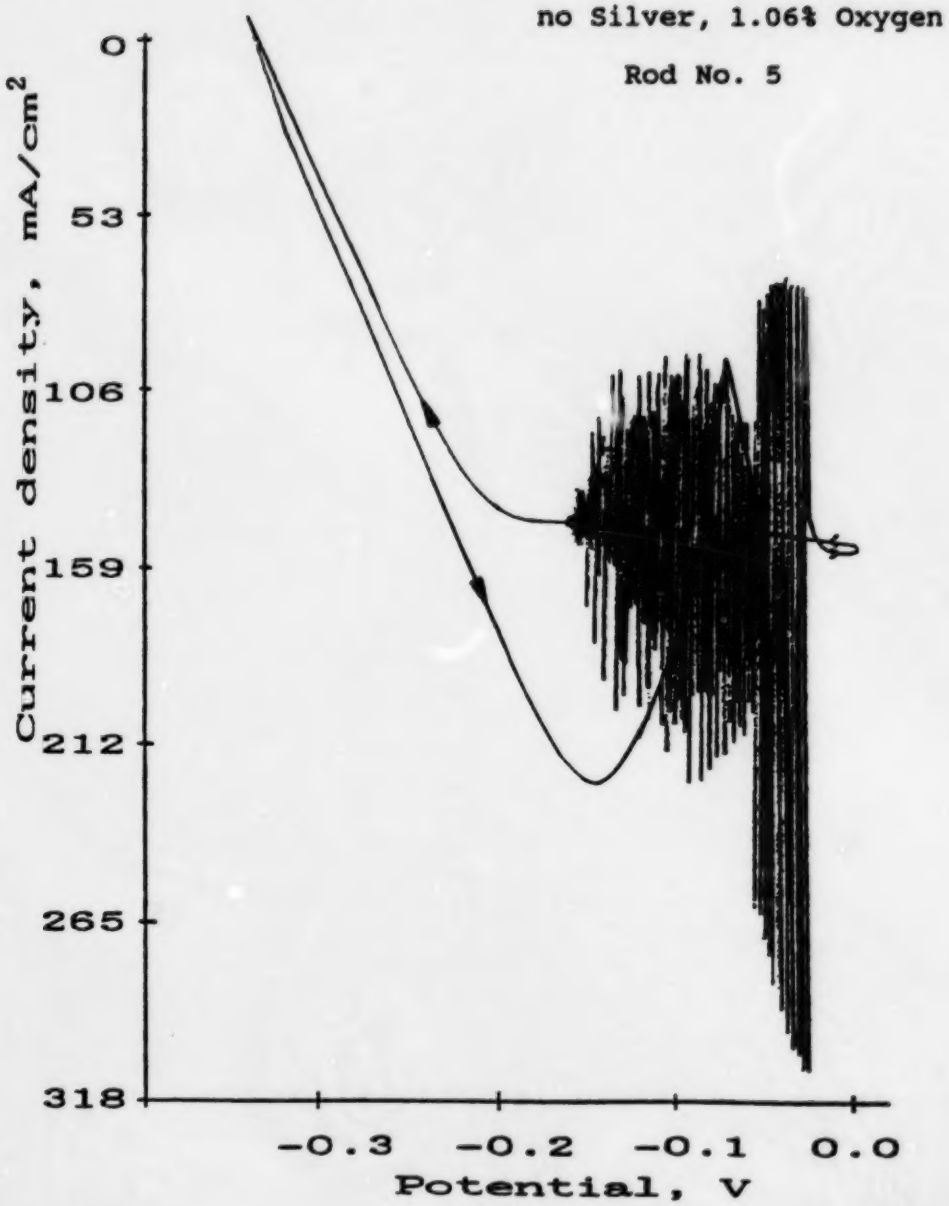


Fig. 16. The cyclic-voltammetry profile of the tenth cycle recorde during continuous cycling.

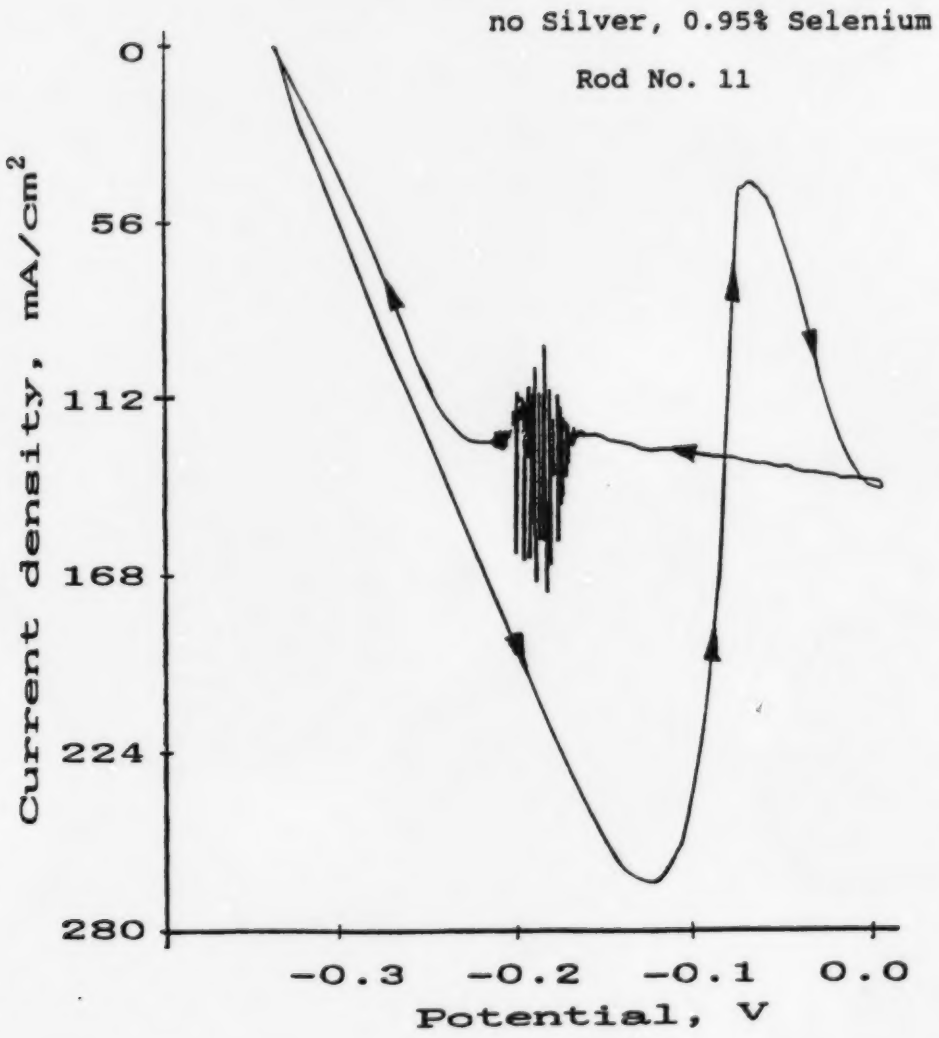


Fig. 17. The cyclic-voltammetry profile of the tenth cycle recorded during continuous cycling.

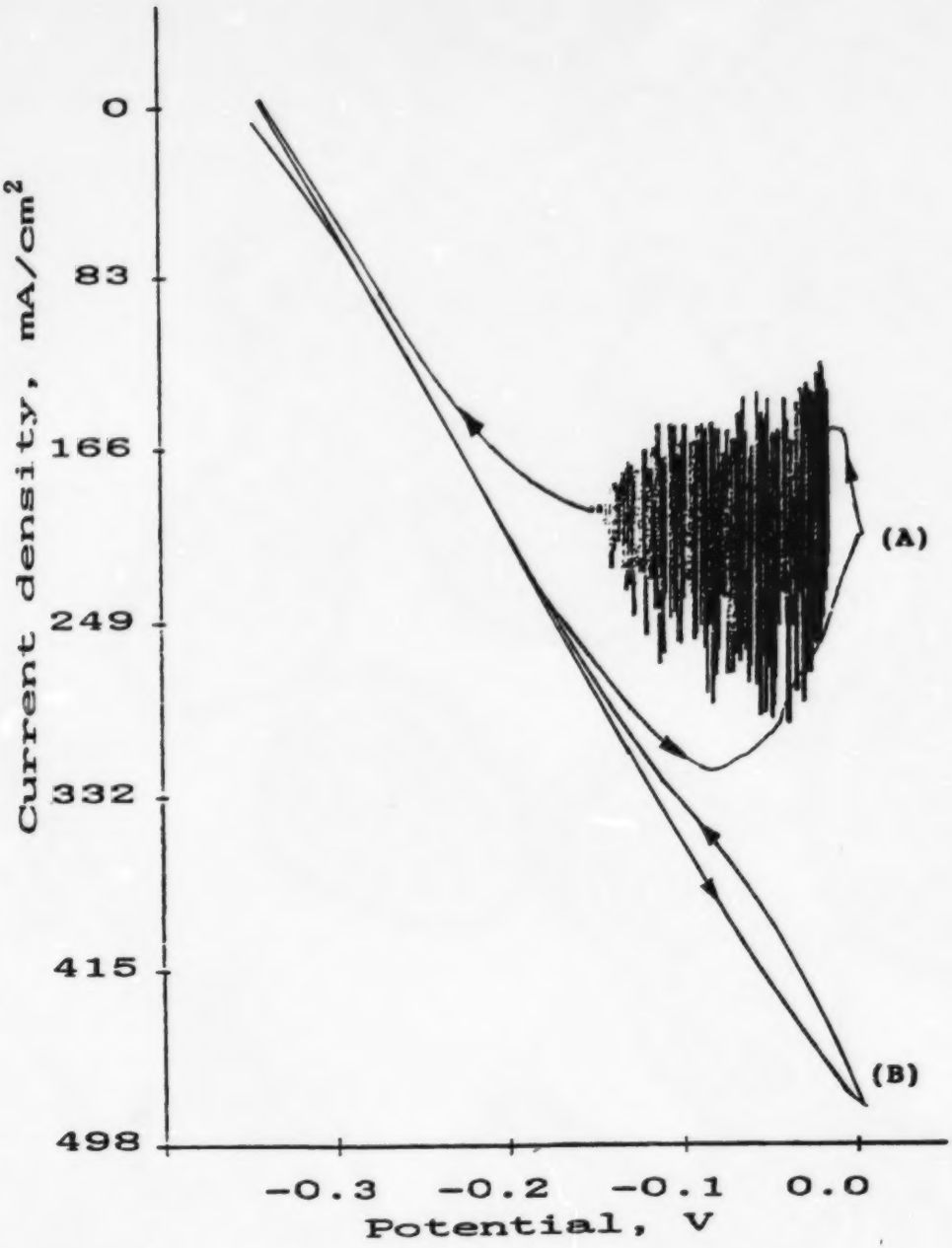


Fig. 18. Cyclic-voltammograms of the copper electrode containing 0.04% Ag (rod No. 21); (A) the 40th cycle of continuous cycling before cleaning, (B) the first cycle after cleaning.

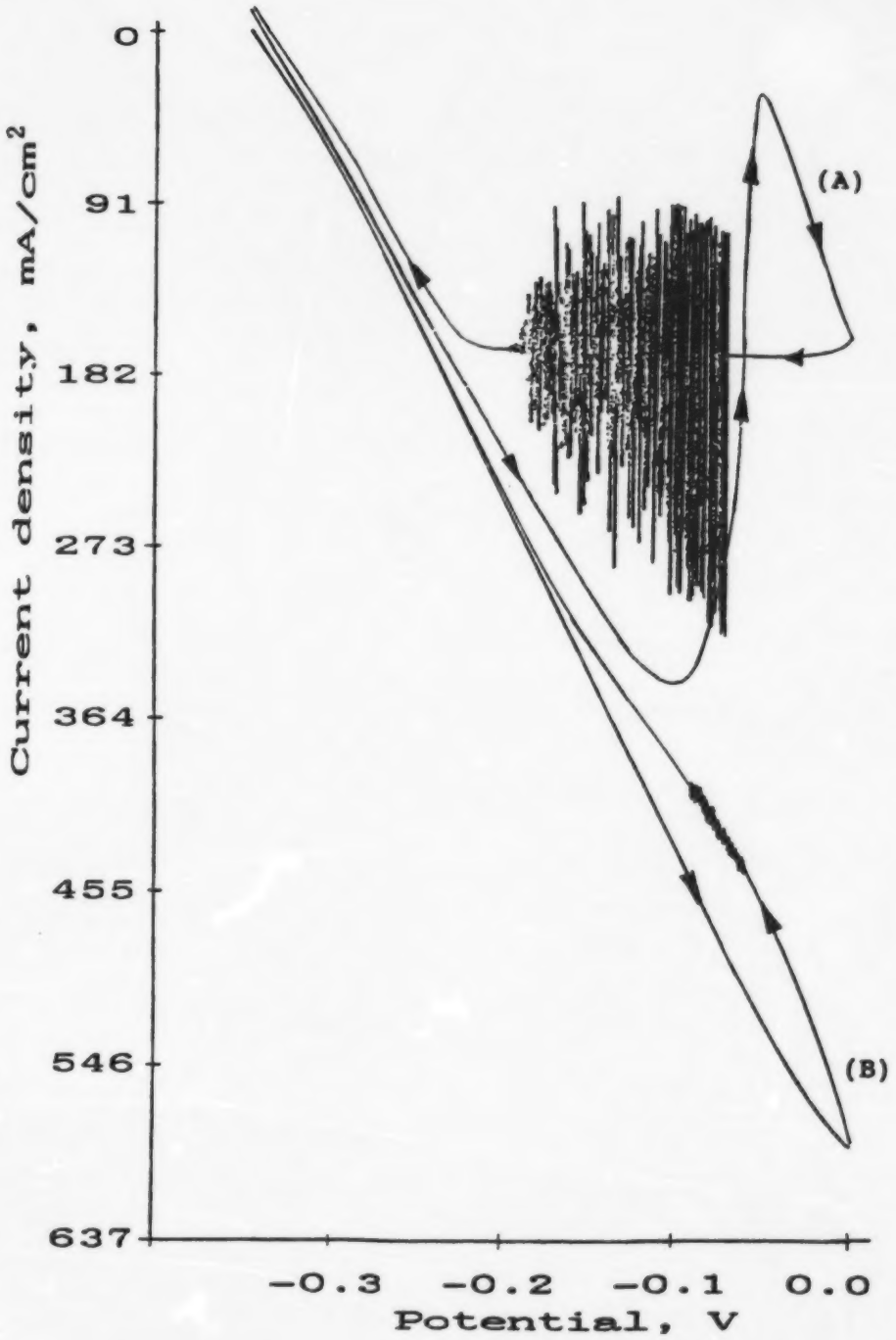


Fig. 19. Cyclic-voltammograms of the copper electrode containing 0.1% Ag (rod No. 6); (A) the 23rd cycle of continuous cycling before cleaning, (B) the first cycle after cleaning.

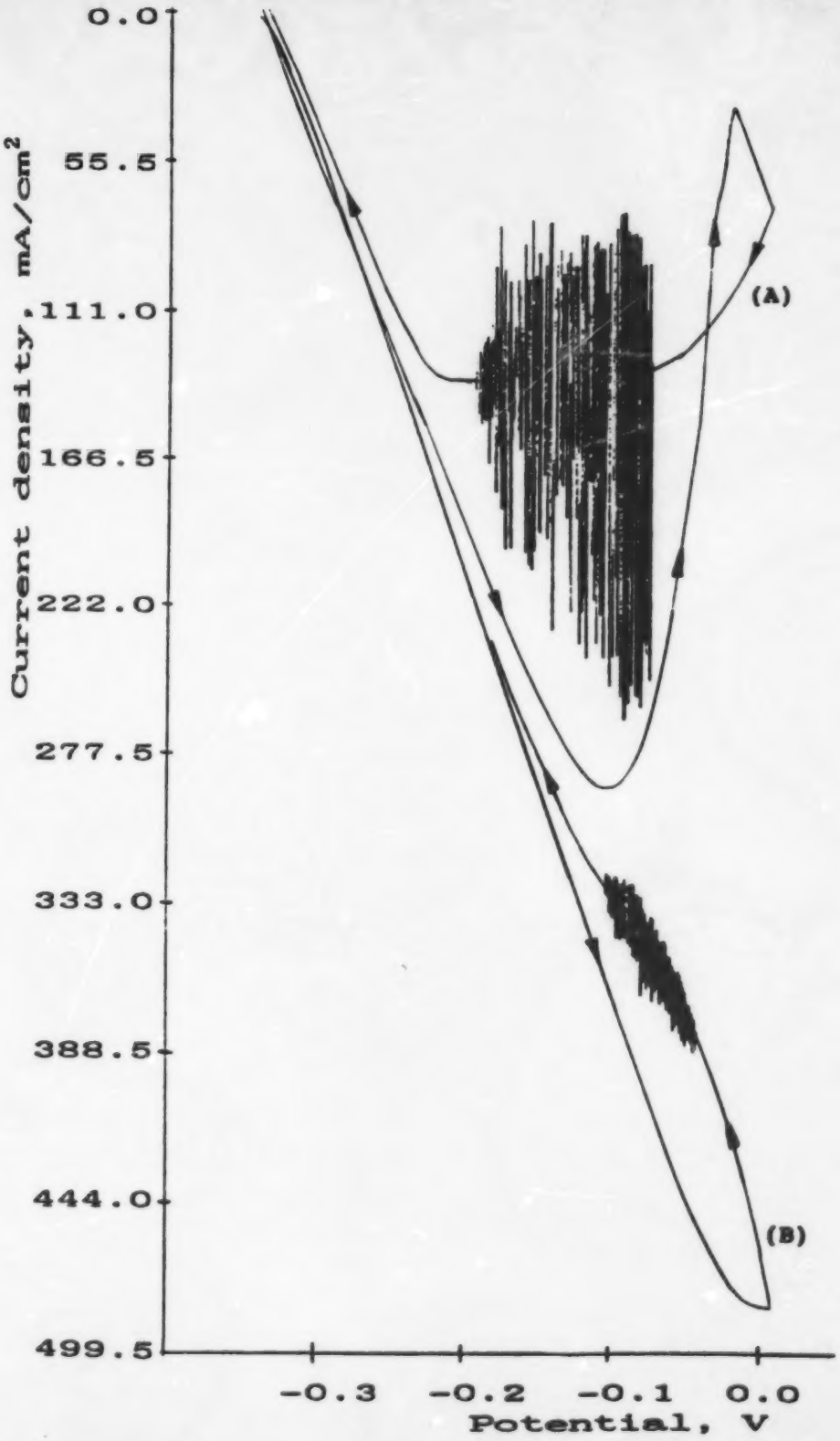


Fig. 20. Cyclic-voltammograms of the copper electrode containing 0.2% Ag (rod No. 22); (A) the 30th cycle of continuous cycling before cleaning, (B) the first cycle after cleaning.

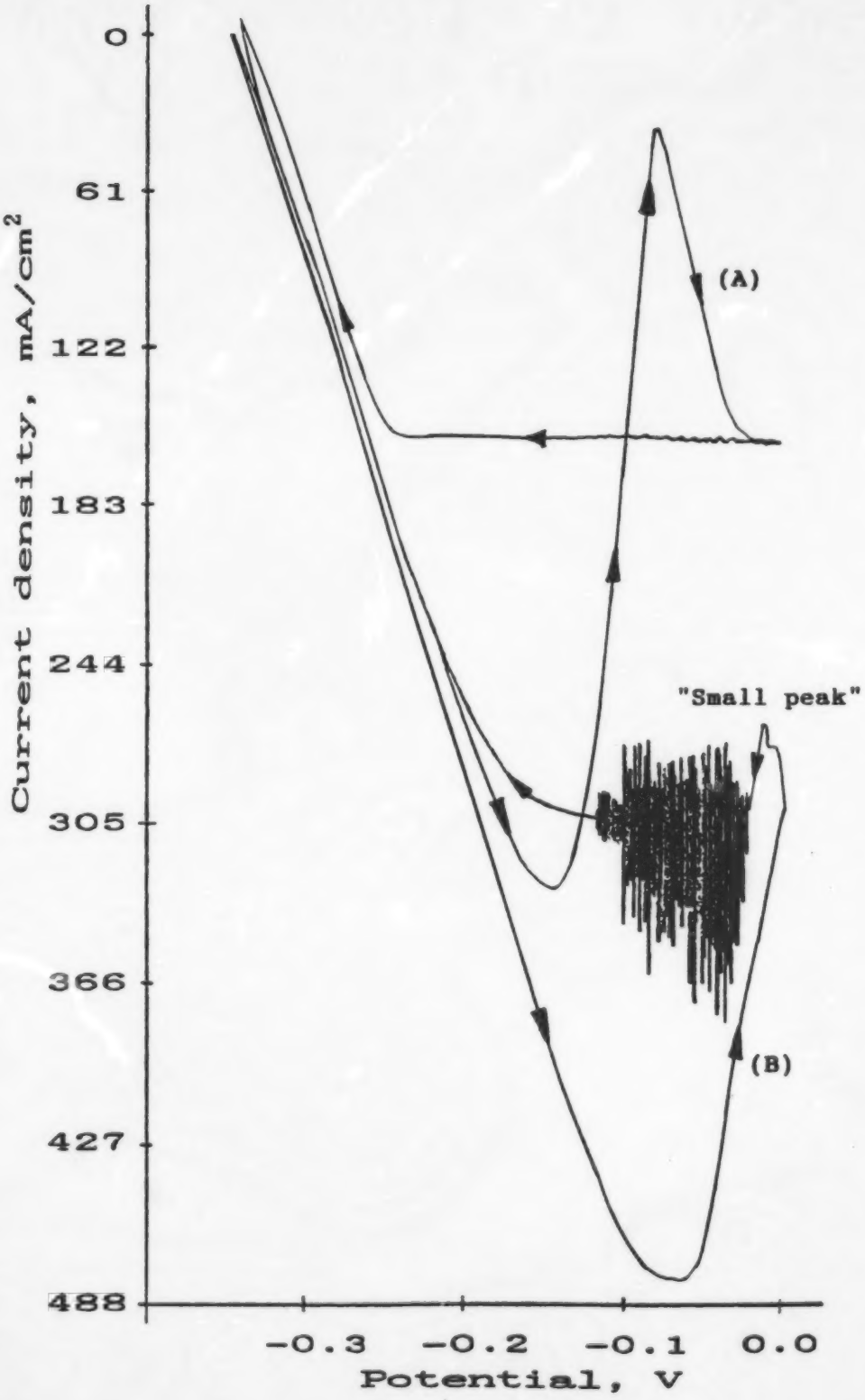


Fig. 21. Cyclic-voltammograms of the copper electrode containing 0.5% Ag (rod No. 7); (A) the 23rd cycle of continuous cycling before cleaning, (B) the first cycle after cleaning.

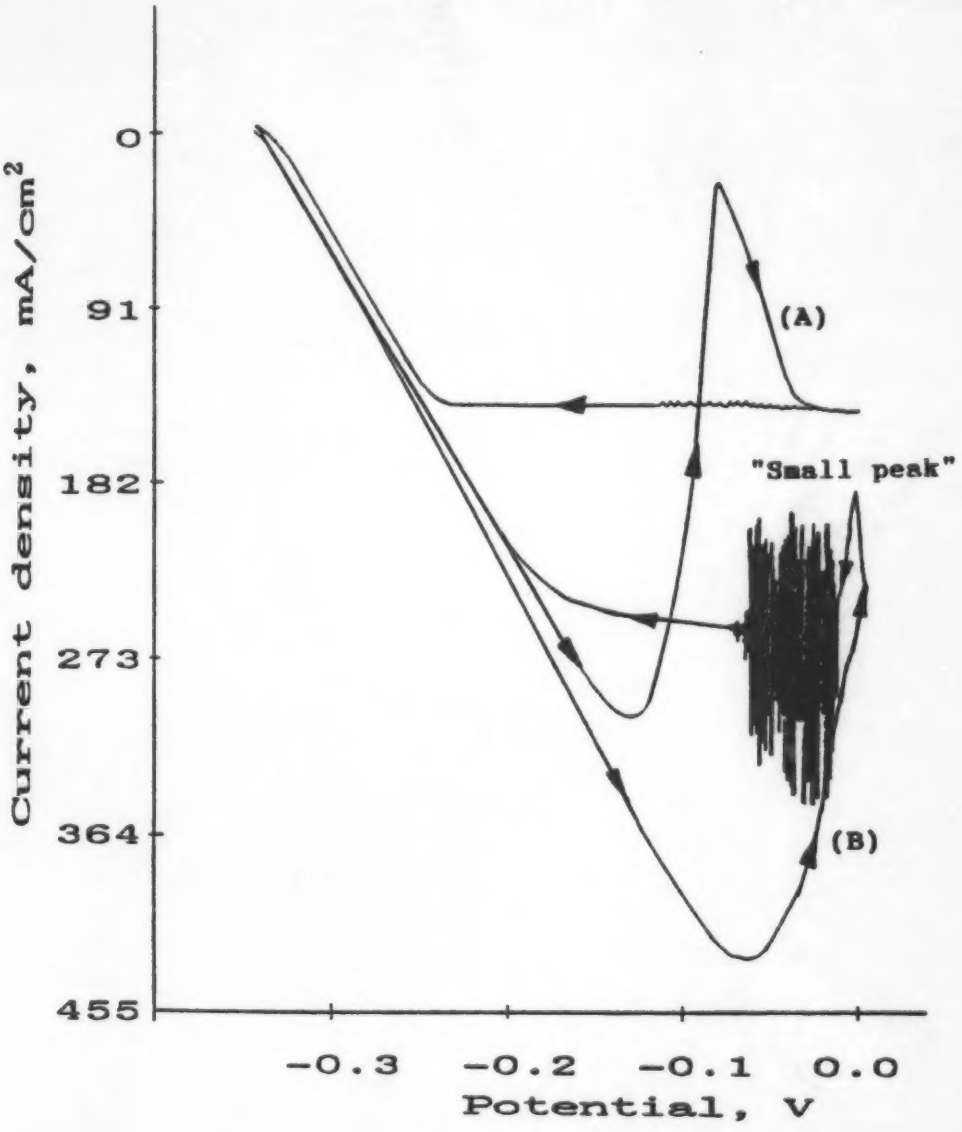


Fig. 22. Cyclic-voltammograms of the copper electrode containing 1.0% Ag (rod No. 8); (A) the 23rd cycle of continuous cycling before cleaning, (B) the first cycle after cleaning.

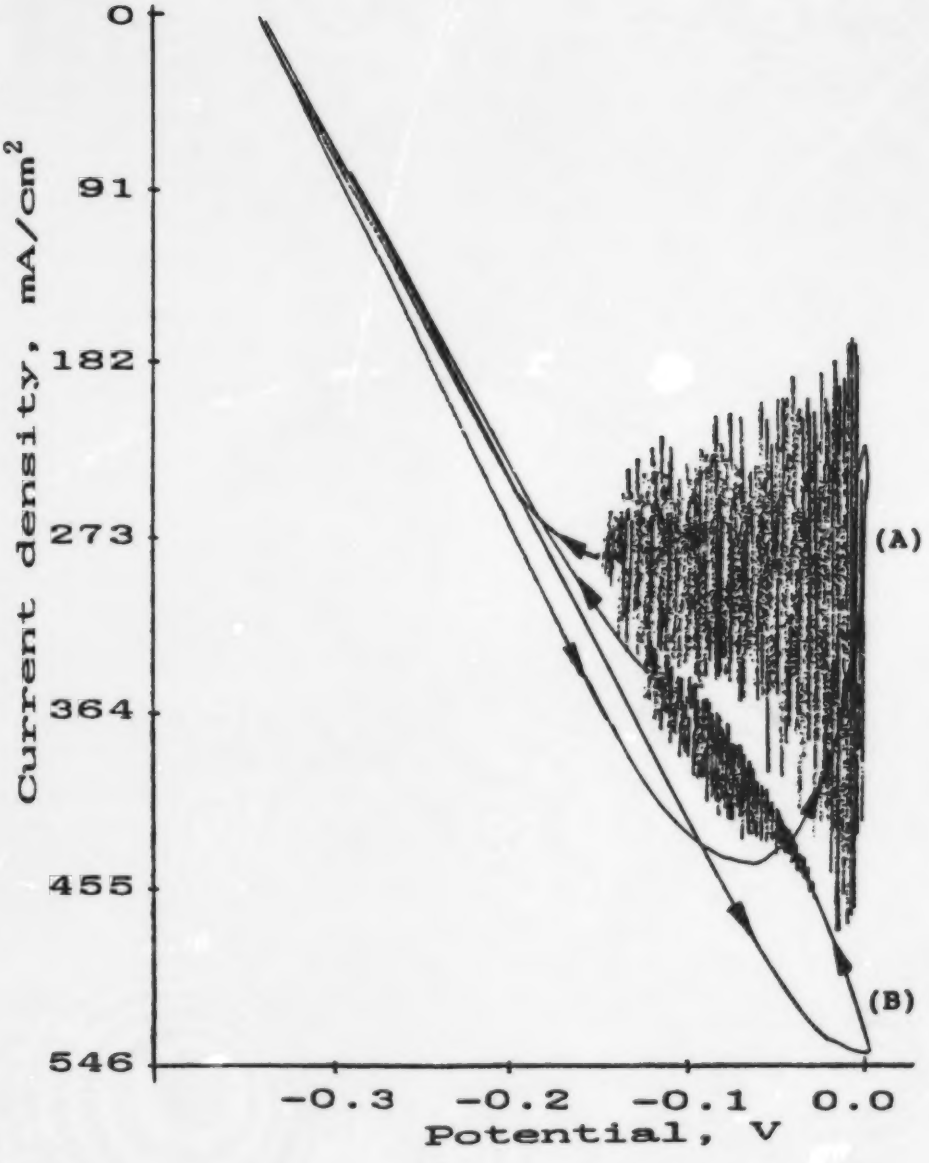


Fig. 23. Cyclic-voltammograms of the copper electrode containin 0.1% Ag (rod No. 6); (A) the 4th cycle of continuous cycling befor cleaning, (B) the 4th cycle of continuous cycling after cleaning

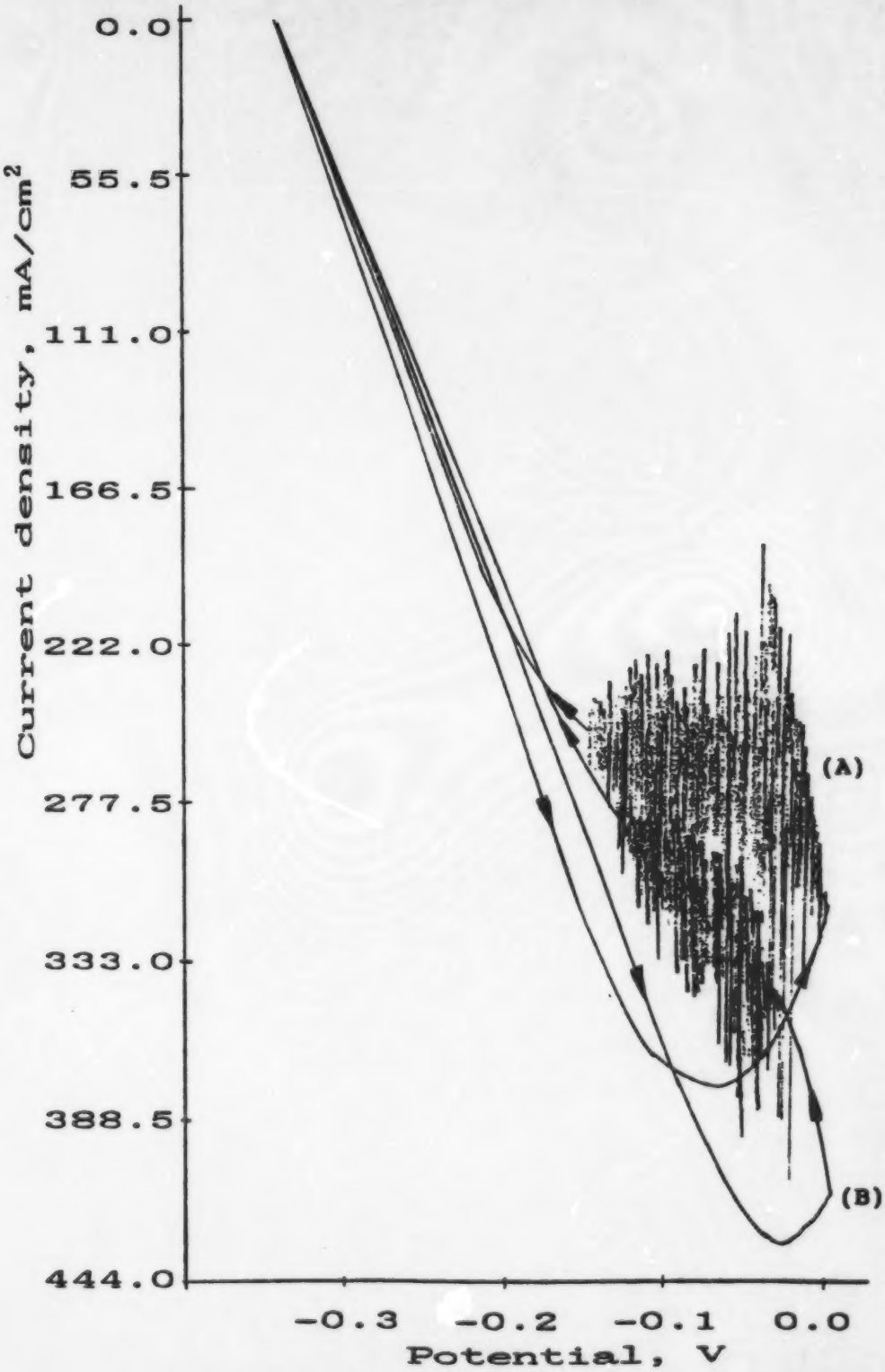


Fig. 24. Cyclic-voltammograms of the copper electrode containing 0.2% Ag (rod No. 22); (A) the 4th cycle of continuous cycling before cleaning, (B) the 4th cycle of continuous cycling after cleaning.

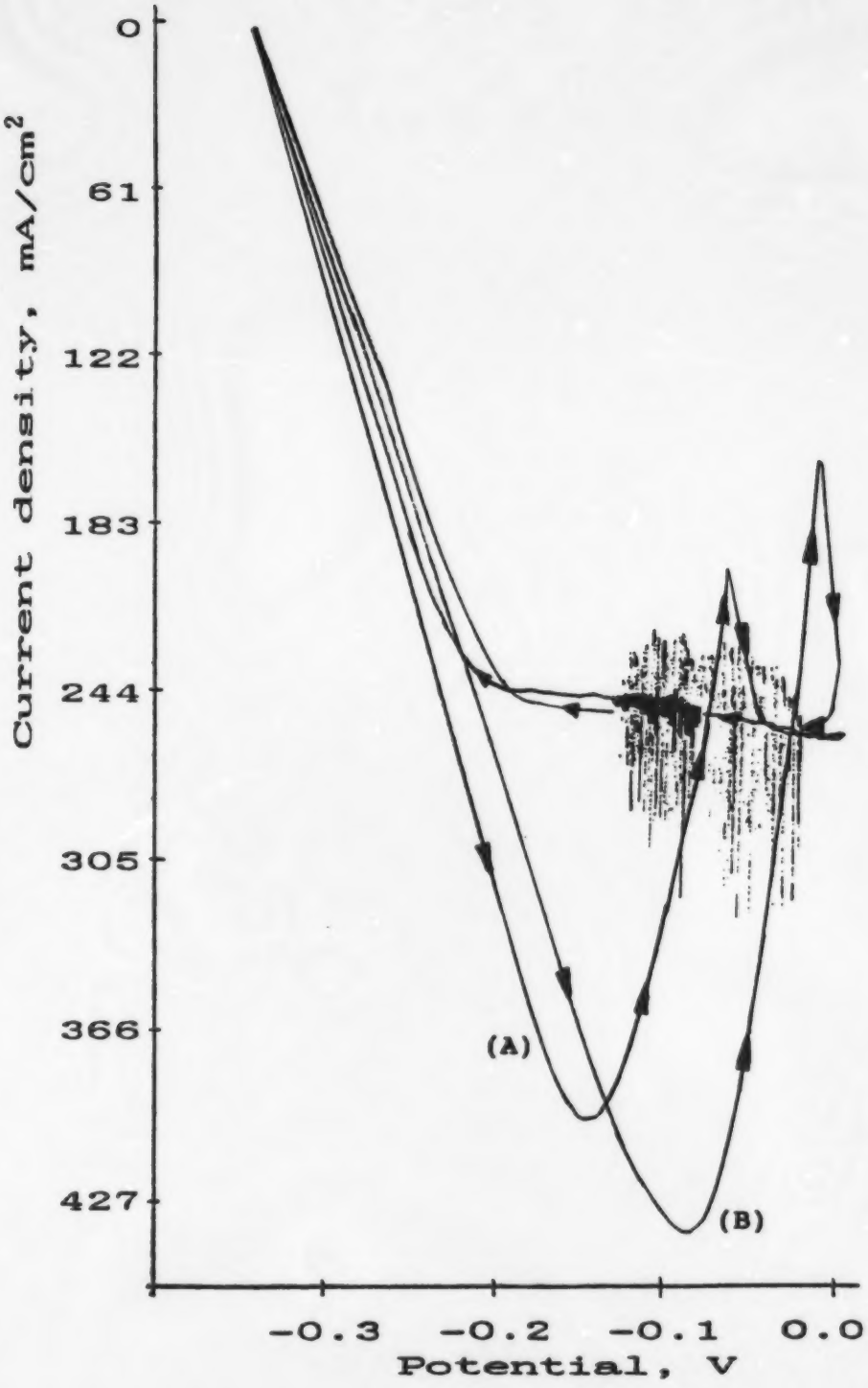


Fig. 25. Cyclic-voltammograms of the copper electrode containing 0.5% Ag (rod No. 7); (A) the 5th cycle of continuous cycling before cleaning, (B) the 5th cycle of continuous cycling after cleaning.

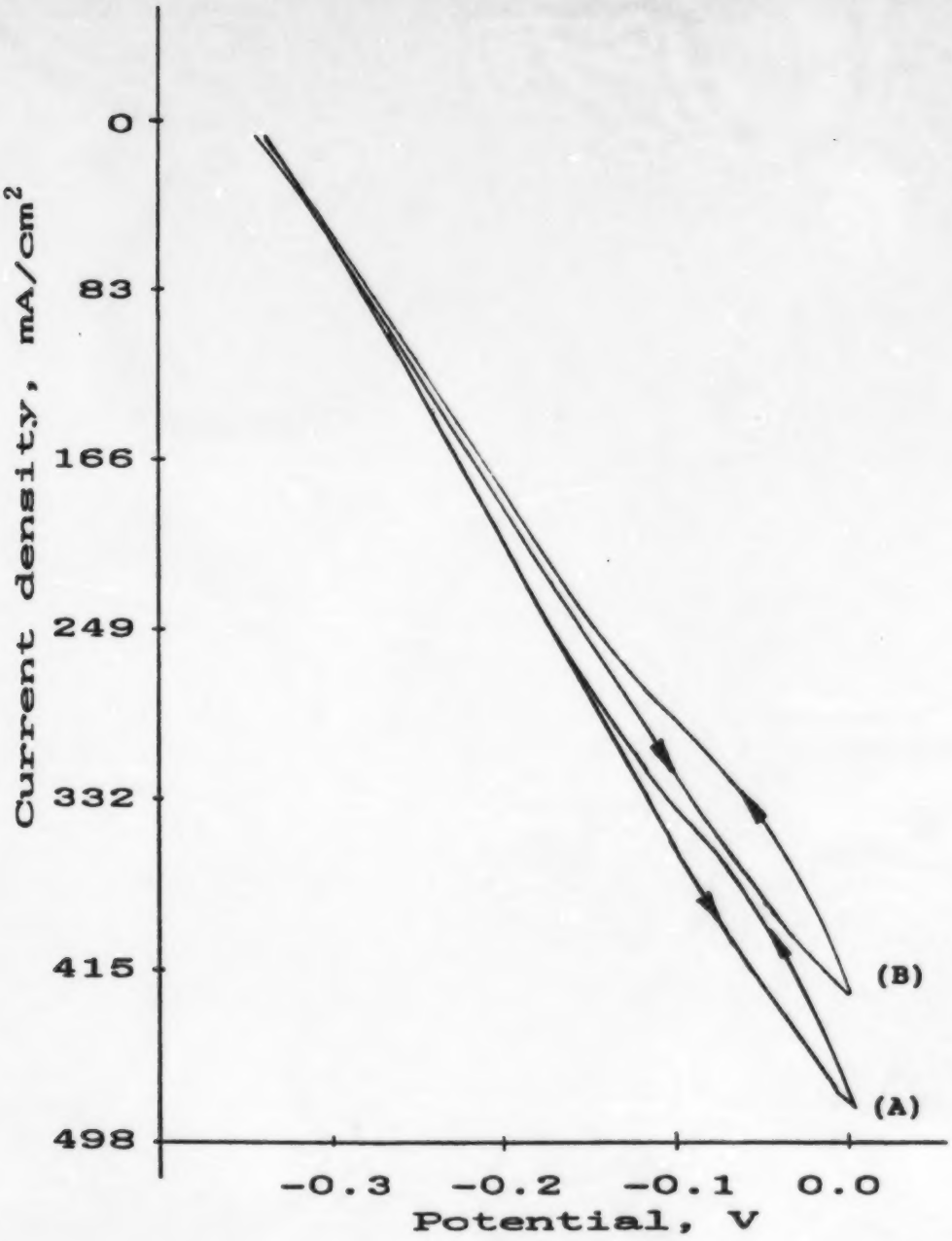
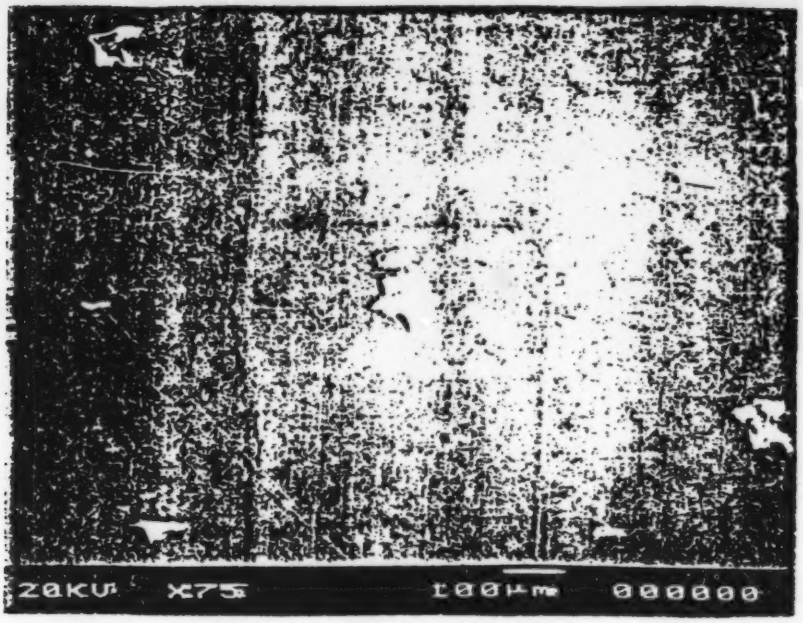


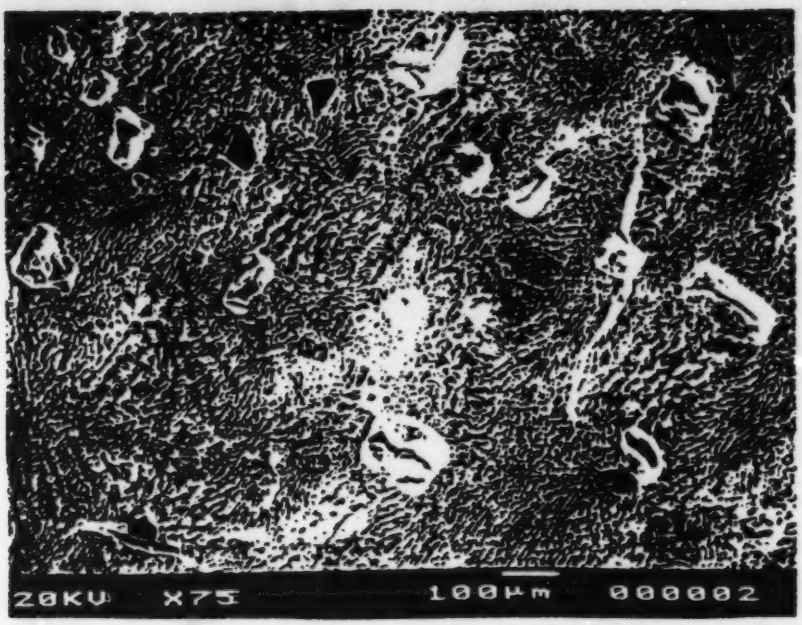
Fig. 26. Cyclic-voltammetry profiles of the copper electrode containing 0.04% Ag (rod No. 21) recorded after cleaning, (A) first cycle, (B) 17th cycle.



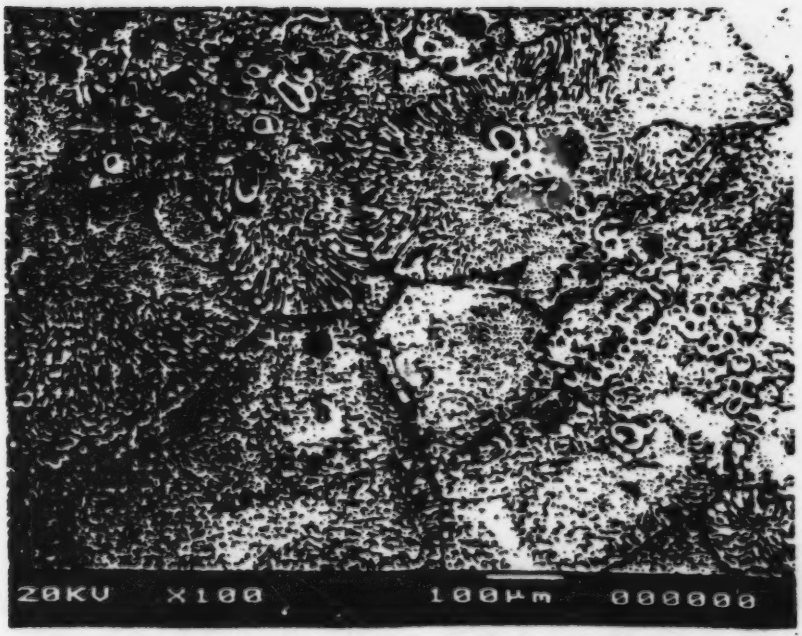
(a)

(b)

Fig. 27. Secondary electron micrographs showing the typical polished surface of: (a) the pure copper anode and (b) the copper anode containing 1.06% oxygen.



(a)



(b)

Fig. 28. Secondary electron micrographs showing the typical washed surface of: (a) the pure copper anode and (b) the copper anode containing 1.06% oxygen; after 40 continuous cycles.

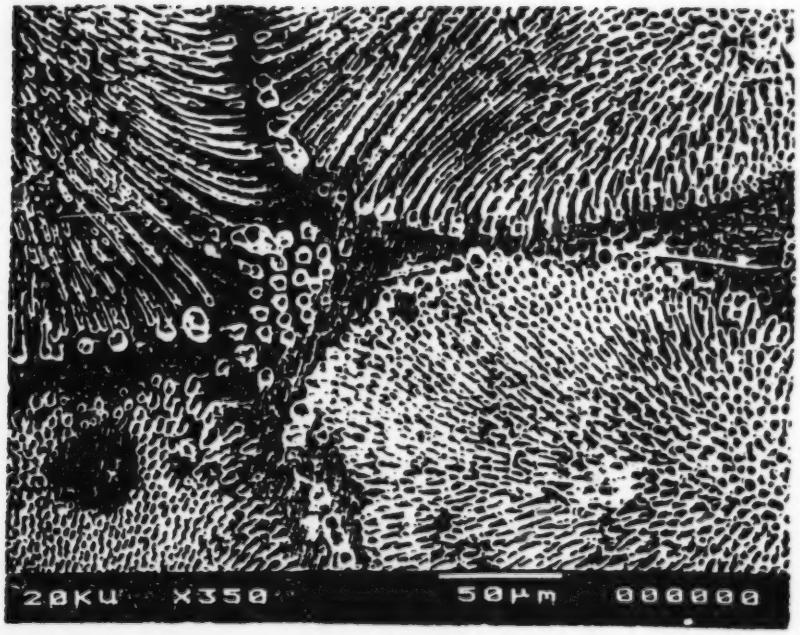
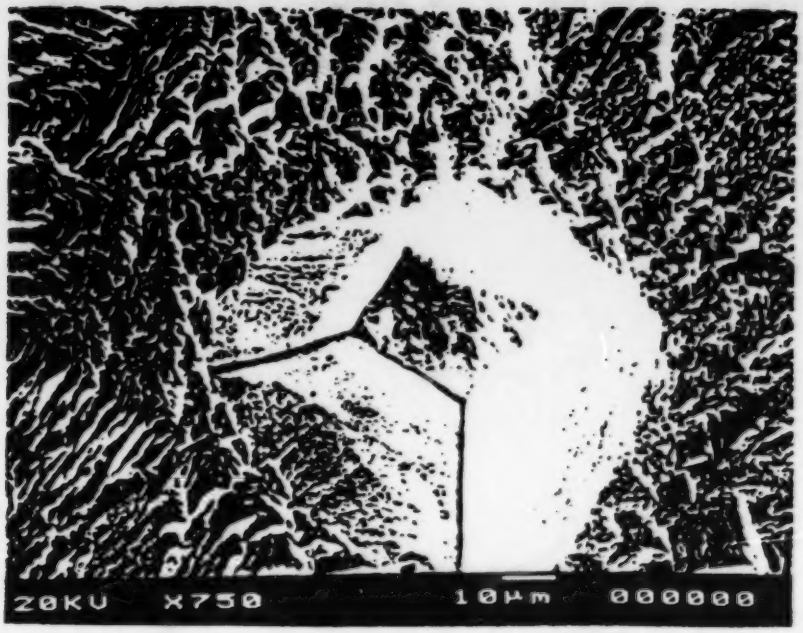
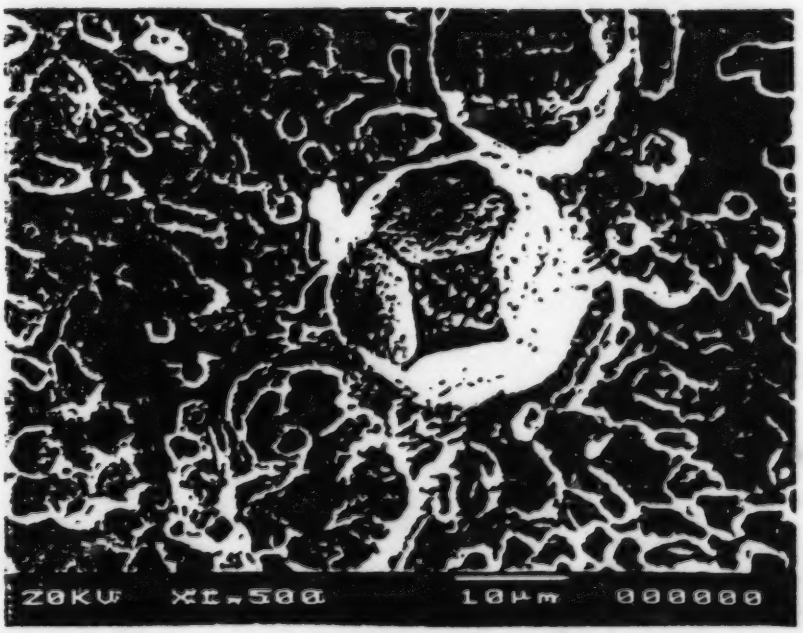


Fig. 29. Secondary electron micrograph showing the detailed morphology of the washed copper anode containing 1.06% oxygen after 40 continuous cycles.



(a)



(b)

Fig. 30. Secondary electron micrographs showing the washed surface of: (a) the pure copper anode and (b) the copper anode containing 1.06% oxygen; after 40 continuous cycles.

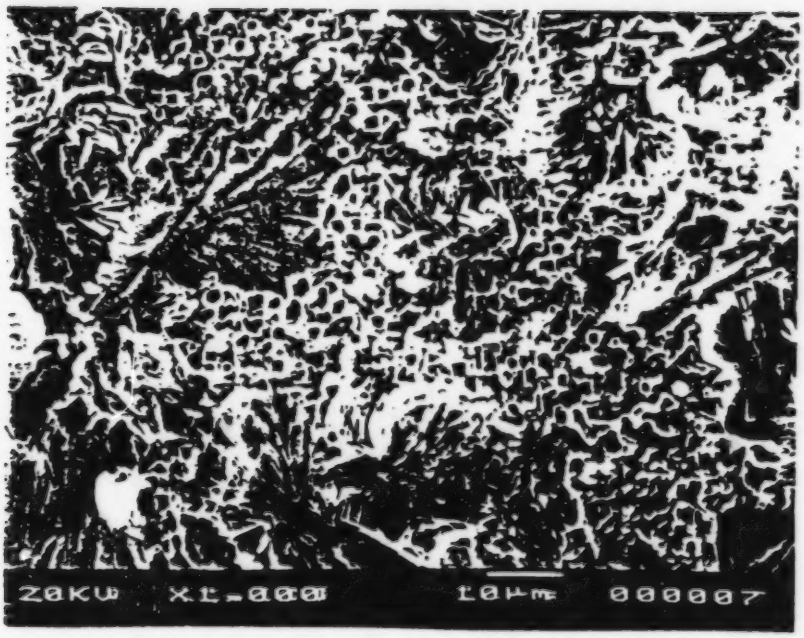


Fig. 31. Secondary electron micrograph showing the unwashed surface of the copper anode containing 1.06% oxygen after 40 continuous cycles.

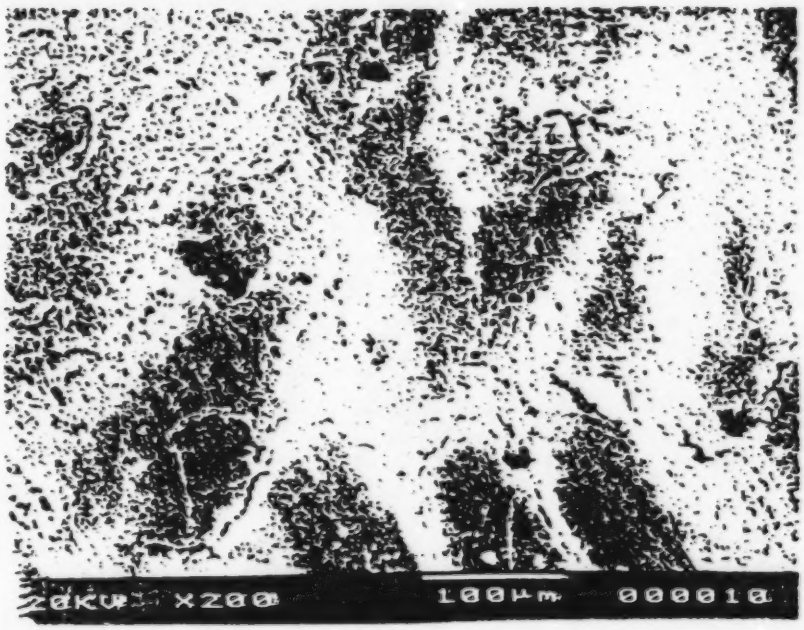


Fig. 32. Secondary electron micrograph showing the unwashed surface of the copper anode containing 0.5% Ag after 30 continuous cycles.